FORM P1

REPUBLIC OF SOUTH AFRICA
PATENTS ACT, 1978
APPLICATION FOR A PATENT AND ACKNOWLEDGEMENT OF RECEIPT
(Section 30(1) - Regulation 39)

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1685

The grant of a Patent is hereby requested by the undermentioned applicant(s) on the present application filed in duplicate

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South Africa translation of WO 98/58974

54 Title of Invention

PROCEDE DE SYNTHESE DE POLYMERES A BLOCS PAR POLYMERISATION RADICALAIRE CONTROLEE

X		The applicant claims priority as set out in the accompaning form P2. The earliest priority claimed is FR 97 07764 23 June 1997	
		This application is for a Patent of Addition to Patent Application No.	24 01
		This application is a fresh application in terms of S 37 and based on Application No.	21 01
		This application is accompanied by:	
	1a	A single copy of a provisional specification of pages	
X	1b	Two copies of a complete specification of 62 pages (in the French Language)	
	2a	Informal drawings of sheets	
	2b	Formal drawings of sheets	
	3.	Publication particulars and abstract (form P8 in duplicate)	
	4.	A copy of Figure of the drawings for the abstract	
	5.	Assignment of invention (from the inventors) or other evidence of title	
	6.	Certified priority documents (documents)	
	7.	Translation of priority documents (documents)	
	8.	Assignment of priority rights	
	9.	A copy of form P2 and the specification of S.A. Patent Application	21 01
	10.	A declaration and power of attorney on form P3	
	11.	Request for ante-dating on form P4	
	12.	Request for classification on form P9	
	13a	Request for delay of acceptance on form P4	
	13b		

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Date 23 June 1998

For the Applicant

The duplicate will be returned to the applicant for service as proof of lodging but is not valid unless endorsed with official stamp.

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FORM P7	REPUBLIC OF SOUTH AFRICA PATENTS ACT, 1978	JOHN & KERNICK P O Box 3511 HALFWAY HOUSE 1685

COMPLETE SPECIFICATION

(Section 30(1) - Regulation 28)

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54 Title of Invention

PROCESS FOR SYNTHESIZING BLOCK POLYMERS BY CONTROLLED RADICAL POLYMERIZATION

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translator to RWS Translations Ltd., of Europa House, Marsham Way, Gerrards Cross, Buckinghamshire, England, hereby declare that I am conversant with the English and French languages and am a competent translator thereof. I declare further that to the best of my knowledge and belief the following is a true and correct translation of the accompanying documents in the French language.

Signed this 10th day of July 1998

RW Gray

R. W. GRAY

For and on behalf of RWS Translations Ltd.

PROCESS FOR SYNTHESIZING BLOCK POLYMERS BY CONTROLLED RADICAL POLYMERIZATION

The present invention relates to a novel radical polymerization process for obtaining block copolymers.

Block polymers are usually prepared by ionic polymerization. This type of polymerization has the drawback of only allowing the polymerization of certain types of non-polar monomers, especially styrene and butadiene, and of requiring a particularly pure reaction mixture and temperatures which are often below room temperature so as to minimize parasitic reactions, and hence of severe operational constraints.

Radical polymerization has the advantage of being easily carried out without having to comply with excessive purity conditions, and at temperatures greater than or equal to room temperature. However, until recently a radical polymerization process allowing block polymers to be obtained did not exist.

Since then, a new radical polymerization process has been developed, namely "controlled" or "living" radical polymerization. Controlled radical polymerization takes place by the growth, by propagation, of macroradicals. These macroradicals, which have a very short lifetime, recombine irreversibly by coupling or dismutation. When the polymerization takes place in the presence of several

comonomers, the compositional variation of the mixture is infinitely slow compared with the lifetime of the macroradical so that the chains have a sequence of random monomer units and not a block-type sequence.

Recently, controlled radical polymerization techniques have been developed in which the ends of polymer chains may be reactivated in the form of a radical by homolytic bond (for example, C-O or C-halogen) scission.

Controlled radical polymerization therefore has the following distinct characteristics:

1. the number of chains is fixed throughout the duration of the reaction,
2. the chains all grow at the same rate, resulting in:
   - a linear increase in the molecular masses with conversion,
   - a narrow distribution of masses,
3. the average molecular mass is controlled by the monomer/chain-precursor molar ratio, and
4. the possibility of preparing block copolymers.

The controlled character is even more pronounced when the rate of reactivation of the chains into radicals is very much greater than the rate of growth of the chains (propagation). There are cases where this is not always true (i.e. the rate of reactivation of the chains into radicals is greater than or equal to the propagation rate) and conditions 1

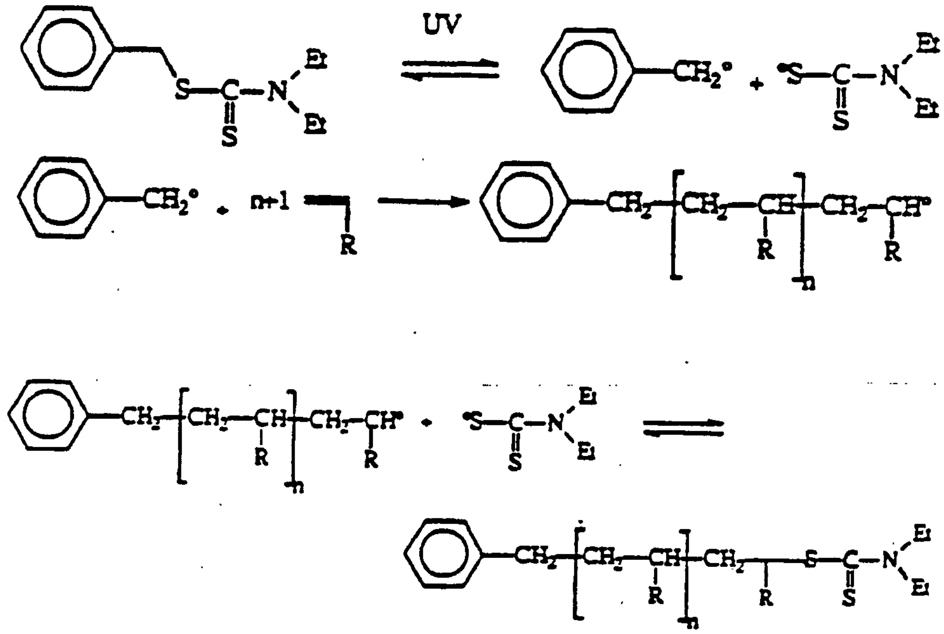
and 2 are not observed, nevertheless it is always possible to prepare block copolymers.

Several approaches have been described for controlling radical polymerization. The most commonly cited consists in introducing, into the mixture, counter radicals which combine reversibly with the growing macroradicals, such as, for example, nitroxyl radicals (Georges *et al.*, *Macromolecules*, **26**, 2987, (1993)). This technique is characterized by high temperatures for labilizing the C-O bond.

Another method, called *Atom Transfer Radical Polymerization*, makes use of transition metal salts combined with organic ligands and an initiator generally consisting of an organic halide; control of the polymerization is made possible by the reversibility of the C-halogen bond (K. Matyjaszewski, *PCT WO 96/30421*). One drawback with this polymerization is that a stoichiometric quantity of metal per chain remains.

Otsu (Otsu *et al.*, *Makromol. Chem. Rapid Comm.*, 3, 127-132, (1982), Otsu *et al. ibid*, **3**, 123-140, (1982), Otsu *et al.*, *Polymer Bull.*, **7**, 45, (1984), *ibid*, **11**, 135, (1984), Otsu *et al*, *J. Macromol. Sci. Chem.*, **A21**, 961, (1984) and Otsu *et al.*, *Macromolecules*, **19**, 2087, (1989)) has shown that certain organic sulphides, particularly dithiocarbamates, allowed chains to be grown in a controlled manner under UV irradiation, according to

the principle:



The principle relies on the photolysis of the C-S bond, which regenerates the carbon macroradical, on the one hand, and the dithiocarbamyl radical, on the other hand. The controlled character of the reaction is due to the reversibility of the C-S bond under UV irradiation. It is thus possible to obtain block copolymers. On the other hand, the equilibrium constant of reaction 1 above is not very large compared with the rate of propagation, this having the consequence of generating relatively broad molecular mass distributions. Thus, the dispersion index ($DI = M_w/M_n$) is between 2 and 5 (Otsu *et al.*, **25**, 7/8, 643-650, (1989)).

Xanthate disulphides and dithiocarbamate disulphides are themselves well known as transfer

agents in conventional radical polymerization in thermal mode and in the presence of an initiator, but no one has hitherto been able to control the polymerization, or even less to produce block copolymers.

Up till now it was known that disulphides (tetraalkylthiuram disulphide, diisopropylxanthate disulphide and mercaptobenzothiazol disulphide) were activatable thermally or under UV irradiation, whereas monosulphides (substituted xanthates, dithiocarbamates) were activatable only under UV irradiation (Roha *et al.*, *Macromol. Symp.*, **91**, 81-92, (1995), and Okawara *et al.*, Bull. of the Tokyo Inst. of Techn., No. 78, 1966).

However, controlled radical polymerization making use of a UV irradiation source is very difficult to carry out from an industrial standpoint since the penetration of the UV photons into the polymerization medium is limited, both by absorption phenomena (most of the ethylenic monomers adsorb in the 210 - 280 nm range) and by diffusion phenomena in disperse media (suspension, emulsion).

Moreover, it has been shown (Turner *et al.*, *Macromolecules*, **23**, 1856-1859, (1990)) that photopolymerization in the presence of dithiocarbamate generates carbon disulphide and may be accompanied by a loss of polymerization control.

For these reasons, it has thus been sought to develop a technique which can be used to obtain block

copolymers by a process without UV irradiation, preferably by thermal initiation.

Until the present time, no controlled radical polymerization system has been able to be demonstrated using dithio compounds in the absence of a UV source.

Controlled radical polymerization has an advantage over conventional radical polymerization when it is a question of preparing functionalized low-molecular-weight chains (reactive telomers). Such polymers are desirable for specific applications such as, for example, coatings and adhesives.

Thus, when it is attempted to synthesize chains grafted with, on average, 2 functional comonomers, the fraction of chains with at most one functional site becomes large when the average degree of polymerization is less than a threshold value (e.g. 20 or 30). Controlled radical polymerization makes it possible to reduce, or even to inhibit, the formation of these oligomers having zero or one functional site which degrade the performance in terms of application.

One object of the present invention is to provide a novel controlled radical polymerization process for the synthesis of block polymers.

Another object of the present invention is to provide a controlled radical polymerization process for the synthesis of block polymers in the absence of a UV source.

Another object is to provide a controlled

radical polymerization process for the synthesis of block polymers from all types of monomers.

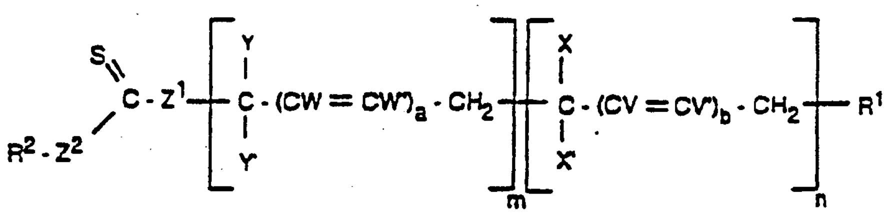
Another object is to provide a controlled radical polymerization process for the synthesis of block polymers containing no metal impurities deleterious to their use.

Another object is to provide a controlled radical polymerization process for the synthesis of block copolymers, the said polymers being chain-end functionalized.

Another object is to provide a controlled radical polymerization process for the synthesis of block polymers and block copolymers having a low polydispersity index.

Another object is to provide a controlled radical polymerization process for the synthesis of oligomers in which the number of functional units is constant from chain to chain.

To this end, the invention relates to a process for polymerizing block polymers of general formula (I):

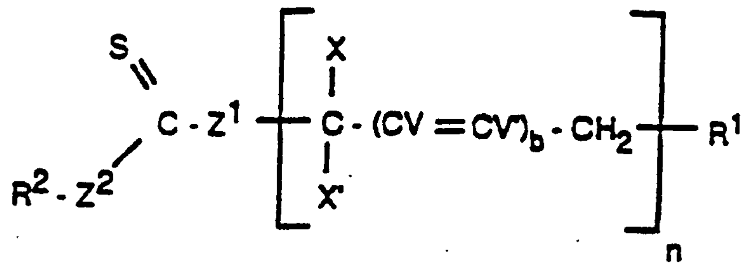


(I)

in which process, the following are brought into contact with each other:

- an ethylenically unsaturated monomer of formula: $CYY'(=CW-CW')_a=CH_2$,

- a precursor compound of general formula (II):



(II)

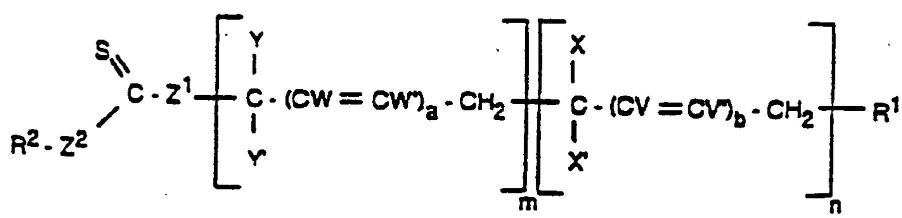
- a radical polymerization initiator.

The invention also relates to the block polymers which can be obtained by the above process.

Finally, the invention relates to polymers of general formula (II), the polydispersity index of which is at most 2.

Further details and advantages of the invention will appear more clearly on reading the description and the examples.

The invention therefore relates first of all to a process for polymerizing block polymers of general formula (I):



(I)

in which:

- Z^1 = S or P,
- Z^2 = O, S or P,
- R^1 and R^2, which are identical or different,

represent:

. an optionally substituted alkyl, acyl, aryl, alkene or alkyne group (i),

or

. an optionally substituted, saturated or unsaturated, carbon or aromatic ring (ii),

or

. an optionally substituted, saturated or unsaturated heterocycle (iii),

it being possible for these groups and rings (i), (ii) and (iii) to be substituted with substituted phenyl groups, substituted aromatic groups, or groups: alkoxycarbonyl or aryloxycarbonyl (-COOR), carboxy (-COOH), acyloxy ($-O_2CR$), carbamoyl ($-CONR_2$), cyano (-CN), alkylcarbonyl, alkylarylcarbonyl, arylcarbonyl, arylalkylcarbonyl, phthalimido, maleimido, succinimido, amidino, guanidimo, hydroxyl (-OH), amino ($-NR_2$), halogen, allyl, epoxy, alkoxy (-OR), S-alkyl, S-aryl, groups having a hydrophilic or ionic character, such as the alkali metal salts of carboxylic acids, the alkali metal salts of sulphonic acid, polyalkylene oxide chains (PEO, PPO), cationic substituents (quaternary ammonium salts),

R representing an alkyl or aryl group,

. a polymer chain,

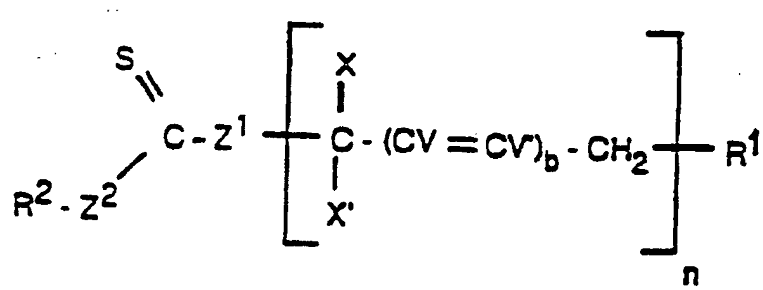
- V, V', W and W', which are identical or different, represent: H, an alkyl group or a halogen,
- X, X', Y and Y', which are identical or different,

represent H, a halogen or an R^3, OR^3, $OCOR^3$, NHCOH, OH, NH_2, NHR^3, $N(R^3)_2$, $(R^3)_2N^+O^-$, $NHCOR^3$, CO_2H, CO_2R^3, CN, $CONH_2$, $CONHR^3$ or $CONR^3_2$ group, in which R^3 is chosen from alkyl, aryl, aralkyl, alkaryl, alkene or organosilyl groups, optionally perfluorinated and optionally substituted with one or more carboxyl, epoxy, hydroxyl, alkoxy, amino, halogen or sulphonic groups,

- a and b, which are identical or different, are equal to 0 or 1,
- m and n, which are identical or different, are greater than or equal to 1 and, when one or other is greater than 1, the individual repeat units are identical or different,

in which process the following are brought into contact with each other:

- an ethylenically unsaturated monomer of formula: $CYY'(=CW-CW')_a=CH_2$,
- a precursor compound of general formula (II):



(II)

- a radical polymerization initiator.

The process therefore consists in bringing into contact with each other a radical polymerization

initiator, an ethylenically unsaturated monomer and a precursor of general formula (II).

The radical polymerization initiator may be chosen from the initiators conventionally used in radical polymerization. These may, for example, be one of the following initiators:

- hydrogen peroxides such as: *tert*-butyl hydroperoxide, cumene hydroperoxide, *tert*-butyl peroxyacetate, *tert*-butyl peroxybenzoate, *tert*-butyl peroxyoctoate, *tert*-butyl peroxyneodecanoate, *tert*-butyl peroxyisobutarate, lauroyl peroxide, *tert*-amyl peroxypivalte, *tert*-butyl peroxypivalate, dicumyl peroxide, benzoyl peroxide, potassium persulphate and ammonium persulphate;

- azo compounds such as: 2-2'-azobis(isobutyronitrile), 2,2'-azobis(2-butanenitrile), 4,4'-azobis(4-pentanoic acid), 1,1'-azobis(cyclohexanecarbonitrile), 2-(*tert*-butylazo)-2-cyanopropane, 2,2'-azobis[2-methyl-N-(1,1)-bis(hydroxymethyl)-2-hydroxyethyl]propionamide, 2,2'-azobis(2-methyl-N-hydroxyethyl)propionamide, 2-2'-azobis(N,N'-dimethyleneisobutyramidine) dichloride, 2,2'-azobis(2-amidinopropane)dichloride, 2,2'-azobis(N,N'-dimethyleneisobutyramide), 2,2'-azobis(2-methyl-N-[1,1-bis(hydroxymethyl)-2-hydroxyethyl]propionamide), 2,2'-azobis(2-methyl-N-[1,1-bis(hydroxymethyl)ethyl]propionamide), 2,2'-

azobis[2-methyl-N-(2-hydroxyethyl)propionamide] and 2,2'-azobis(isobutyramide) dihydrate;

- redox systems including combinations such as:

. mixtures of hydrogen peroxide or alkyl peroxide, peresters, percarbonates and the like and of any one of the salts of iron, titanous salts, zinc formaldehyde sulphoxylate or sodium formaldehyde sulphoxylate, and reducing sugars;

. alkali-metal or ammonium persulphates, perborate or perchlorate in combination with an alkali metal bisulphite, such as sodium metabisulphite, and reducing sugars;

. alkali-metal persulphate in combination with an arylphosphinic acid, such as benzenephosphonic acid and other similar acids, and reducing sugars.

The amount of initiator to be used is determined so that the amount of radicals generated is at most 20 mol% with respect to the amount of compound (II), preferably at most 5 mol%.

As **ethylenically unsaturated monomer**, the monomers chosen from styrene or its derivatives, butadiene, chloroprene, (meth)acrylic esters, vinyl esters and vinyl nitriles are more specifically used according to the invention.

Butadiene and chloroprene correspond to the case in which a and b = 1 in the formulae (I), (II) and in the formula for the monomer given above.

"(Meth)acrylic esters" should be understood to mean esters of acrylic acid and of methacrylic acid with hydrogenated or fluorinated C_1-C_{12}, preferably C_1-C_8, alcohols. Among compounds of this type, mention may be made of: methyl acrylate, ethyl acrylate, propyl acrylate, n-butyl acrylate, isobutyl acrylate, 2-ethylhexyl acrylate, tert-butyl acrylate, methyl methacrylate, ethyl methacrylate, n-butyl methacrylate and isobutyl methacrylate.

The vinyl nitriles include more particularly those having from 3 to 12 carbon atoms, such as, in particular, acrylonitrile and methacrylonitrile.

It should be noted that styrene may be replaced, completely or partly, by derivatives such as alpha-methylstyrene or vinyltoluene.

The other ethylenically unsaturated monomers which can be used, alone or as mixtures, or which can be copolymerized with the above monomers, are, for example:

- vinyl esters of carboxylic acids, such as vinyl acetate, vinyl versatate and vinyl propionate;
- vinyl halides;
- ethylenically unsaturated monocarboxylic and dicarboxylic acids, such as acrylic acid, methacrylic acid, itaconic acid, maleic acid and fumaric acid, and monoalkyl esters of dicarboxylic acids of the type mentioned with alkanols preferably having from 1 to 4 carbon atoms and their N-substituted

derivatives;

- amides of unsaturated carboxylic acids, such as acrylamide, methacrylamide, N-methylolacrylamide or methacrylamide, and N-alkylacrylamides;

- ethylenic monomers containing a sulphonic acid group and its ammonium or alkali metal salts, for example vinylsulphonic acid, vinylbenzenesulphonic acid, alpha-acrylamidomethylpropanesulphonic acid and 2-sulphoethylene methacrylate;

- amides of vinylamine, especially vinylformamide or vinylacetamide; and

- unsaturated ethylenic monomers containing a secondary, tertiary or quaternary amino group, or a heterocyclic group containing nitrogen, such as, for example, vinylpyridines, vinylimidazole, aminoalkyl (meth)acrylates and aminoalkyl (meth)acrylamides such as dimethylaminoethyl acrylate or methacrylate, di-*tert*-butylaminoethyl acrylate or methacrylate and dimethylaminomethylacrylamide or dimethylaminomethacrylamide. Likewise, it is possible to use zwitterionic monomers such as, for example, sulphopropyl(dimethyl)aminopropyl acrylate.

In order to prepare the copolymers of formula (I) for which Y = H and Y' = NH_2, it is preferred to use as ethylenically unsaturated monomers the amides of vinylamine, for example vinylformamide or vinylacetamide. The copolymer obtained is then

hydrolysed to acid or basic pH.

In order to prepare the copolymers of formula (I) for which Y = H and Y' = OH, it is preferred to use as ethylenically unsaturated monomers vinyl esters of carboxylic acid such as, for example, vinyl acetate. The copolymer obtained is then hydrolysed to acid or basic pH.

The types and amounts of copolymerizable monomers employed according to the present invention vary depending on the particular final application for which the block polymer is intended. These variations are well known and may be easily determined by those skilled in the art.

In order for the polymer of general formula (I) to be a block polymer, the **"precursor" compound of general formula (II)** must be a polymer.

Thus, n is greater than or equal to 1, preferably greater than or equal to 6. The monomer units of this polymer may be identical or different.

According to the preferred embodiment of the invention, in the formula (II) for the precursor compounds, Z^1 is a sulphur atom and Z^2 is an oxygen atom; these compounds are therefore chain-end functionalized by alkyl xanthates.

Preferably, in the formula (II) for the precursor compounds, R^1 represents:

- a group of formula $CR'^1R'^2R'^3$ in which:

. R'^1, R'^2 and R'^3 represent groups (i), (ii) or (iii)

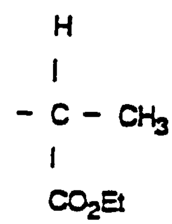
as defined above or

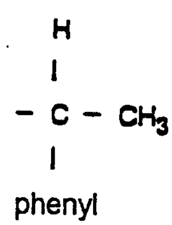
. $R'^1 = R'^2 = H$ and R'^3 is an aryl, alkene or alkyne group,

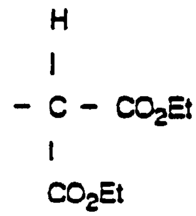
- or a $-COR'^4$ group in which R'^4 represents a group (i), (ii) or (iii) as defined above.

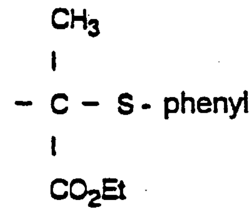
Likewise, in the formula (II) for the precursor compounds, R^2 preferably represents a group of formula: $-CH_2R'^5$, in which R'^5 represents H or a group (i), (ii) or (iii) with the exception of aryl, alkyne and alkene groups.

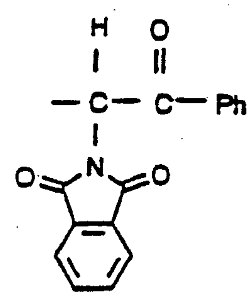
The most interesting results have been obtained for compounds of formula (II) when Z^1 is a sulphur atom, Z^2 is an oxygen atom, R^2 is an ethyl or phenyl group and R^1 is a group chosen from:











The R^1 group may also represent a polymer chain coming from a radical or ionic polymerization or coming from a polycondensation.

The compounds (II) particularly preferred are styrene (Y' = H, Y = C_6H_5, b = 0), methyl acrylate (Y' = H, Y = COOMe, b = 0), ethyl acrylate (Y' = H, Y = COOEt, b = 0), butyl acrylate (Y' = H, Y = COOBu, b = 0), *tert*-butyl acrylate (Y' = H, Y = COOtBu, b = 0), vinyl acetate (Y' = H, Y = OCOMe, b = 0) and acrylic acid (Y' = H, Y = COOH, b = 0) homopolymers, for which:

- Z^1 = S, Z^2 = O, R^1 = CHCH3(CO_2Et) and R^2 = Et, or
- Z^1 = S, Z^2 = O, R^1 = $CH(CO_2Et)_2$ and R^2 = Et.

This precursor polymer (II) may come from the radical polymerization of an ethylenically unsaturated monomer of formula: $CXX'(=CV-CV')_b=CH_2$ by bringing the said monomer into contact with a radical polymerization initiator and a compound of general formula (III), (IV) or (V):

$$R^2-Z^2-\underset{}{C}(=S)-Z^1-R^1 \qquad \text{(III)}$$

$$R^2\!\left(-Z^2-\underset{\displaystyle \overset{\|}{S}}{C}-Z^1-R^1\right)_p \qquad \text{(IV)}$$

$$R^1\!\left(-Z^1-\underset{\displaystyle \overset{\|}{S}}{C}-Z^2-R^2\right)_p \qquad \text{(V)}$$

p being between 2 and 10, preferably between 2 and 5.

In this synthesis, the radical polymerization initiators and the ethylenically unsaturated monomers are of the type previously mentioned.

With regard to the compounds of general formulae (III), (IV) or (V), the symbols R^2, Z^2, R^1 and Z^1 have the same meaning as previously. As regards their symbols, the preferred ones are the same as previously.

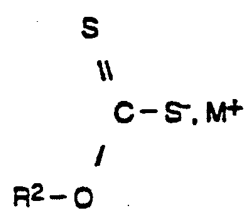
Thus, the preferred compounds of general formula (III) are ethyl α-(O-ethylxanthyl)propionate (Z^1 = S, Z^2 = O, R^1 = $CH(CH_3)(CO_2Et)$, R^2 = Et) and

[1-(O-ethylxanthyl)malonate (Z^1 = S, Z^2 = O, R^1 = $CH(CO_2Et)_2$, R^2 = Et).

Among compounds of formula (IV), those for which R^2 is the $-(CH_2)_q$-group or a polyether group $-(CHR-CH_2-O)_q-CHR-CH_2-$, with q between 2 and 10, are preferred.

Among the compounds of formula (V), those for which R^1 is the group $-CH_2$-phenyl-CH_2- or the group $-CHCH_3CO_2CH_2CH_2CO_2CHCH_3-$ are preferred.

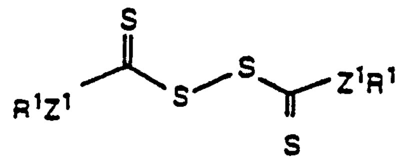
The compounds of formulae (III), (IV) and (V) are readily accessible. Those for which Z^1 is a sulphur atom and a Z^2 is an oxygen atom, called alkyl xanthates, may in particular be obtained by reaction between a xanthate salt, such as an alkali metal salt of the type:



and a halogenated derivative of the type: Hal-R^1, with Hal chosen from Cl, Br or I.

The compounds of formulae (III), (IV) and (V), in which Z^1 is S, may also be obtained by the process in which the following are mixed and heated:

- a disulphide (S) compound of formula (A):



- and a diazo (N) compound of formula (B):

$$R^2Z^2 - N = N - Z^2R^2$$

The complete process of synthesizing a block polymer of formula (I) according to the invention may therefore consist in:

(1) synthesizing a polymer by bringing into contact with each other an ethylenically unsaturated monomer of formula $(CXX'(=CV-CV')_b=CH_2$, a radical polymerization initiator and a compound of formula (III), (IV) or (V), and

(2) using the polymer obtained as precursor of general formula (II) in order to prepare a diblock polymer by bringing it into contact with a new ethylenically unsaturated monomer of formula: $CYY'(=CW-CW')_a=CH_2$ and a radical polymerization initiator.

This step (2) may be repeated as many times as desired using new monomers to synthesize new blocks and to obtain a multiblock polymer.

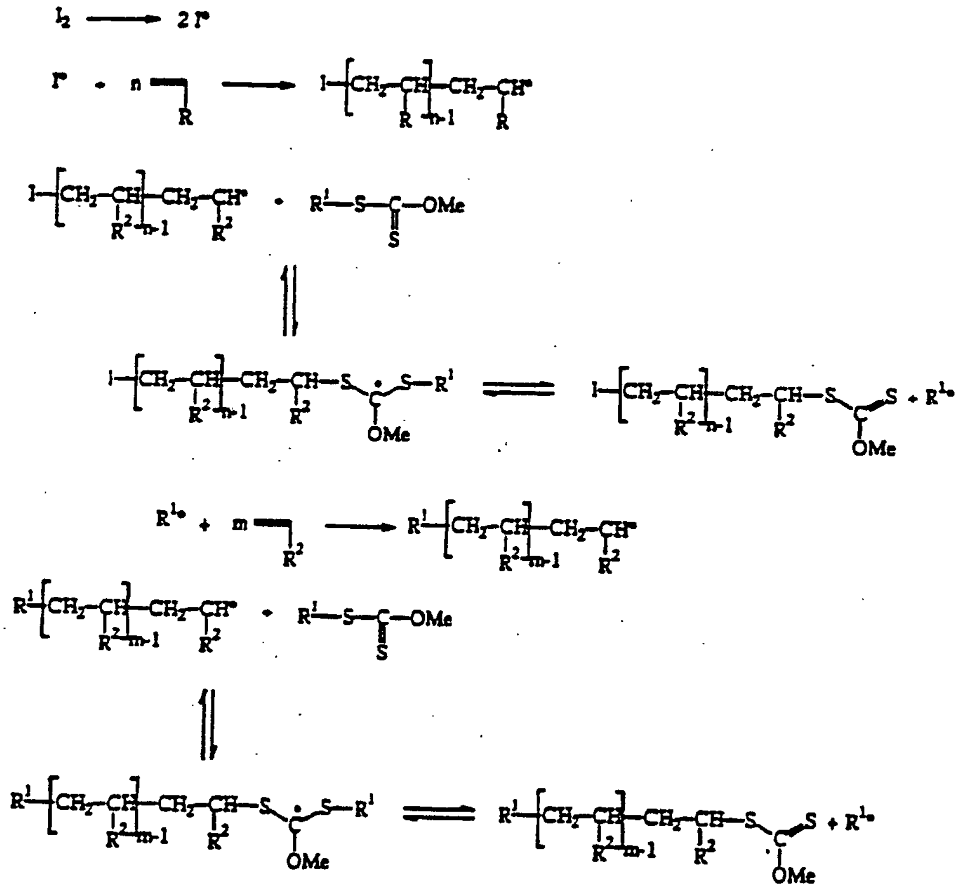
As indicated previously, for the preparation of precursors of formula (II) for which X = H and X' = NH_2 (step (1) defined above), it is preferred to use, as

ethylenically unsaturated monomers, amides of vinylamine, for example vinylformamide or vinylacetamide. The polymer obtained is then hydrolysed to acid or basic pH.

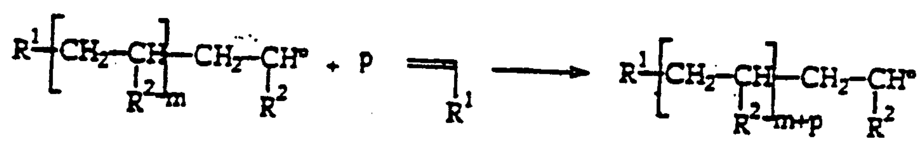
Likewise, for the preparation of precursors of formula (II) for which X = H and X′ = OH, it is preferred to use vinyl esters of carboxylic acids, such as vinyl acetate for example, as ethylenically unsaturated monomers. The polymer obtained is then hydrolysed to acid or basic pH.

Without thereby excluding any other reaction scheme, the presumed action mechanism of the polymerization is illustrated below in the case of a xanthate-type precursor compound of formula (II).

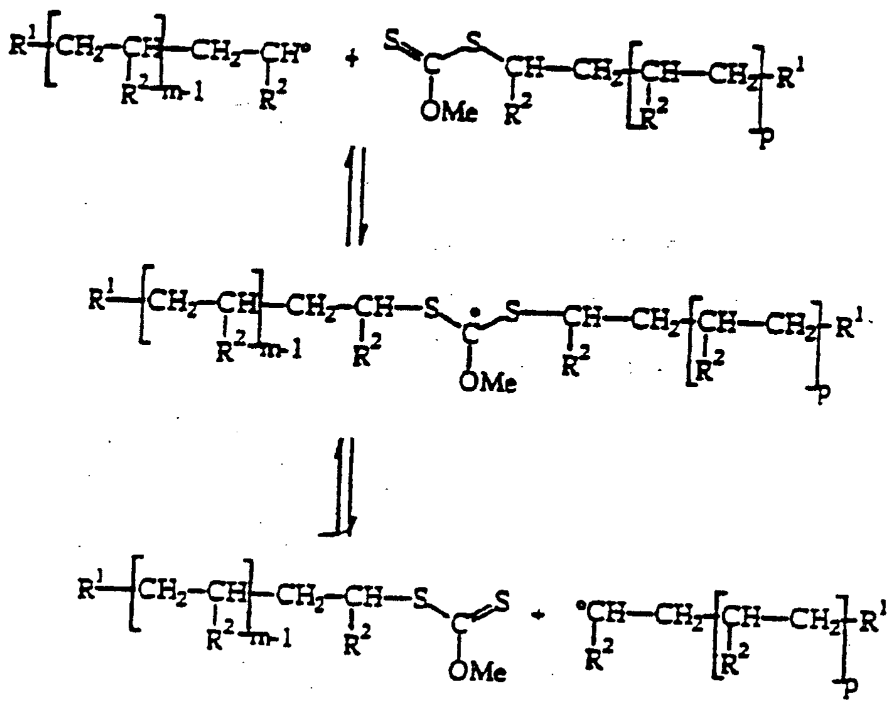
1. Initiation of the polymerization:



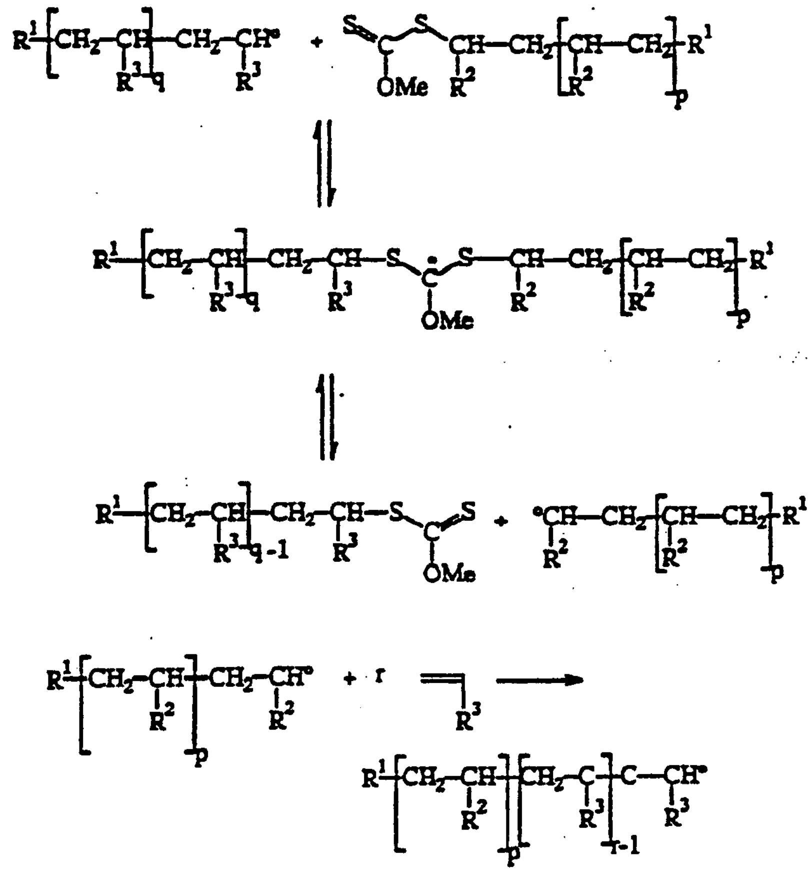
2. Chain growth



3. Degenerative chain transfer



The degenerative chain transfer reaction makes it possible to react a "dormant" chain carrying the xanthate unit at its end into a macroradical. This unit may grow by propagation and again be added onto a xanthate chain end, and fragment. When the xanthate exchange rate is at least as great as the propagation rate the chains will then grow according to a controlled process. When the CH_2=CHR^2 monomer is completely consumed, a second monomer of a different type, CH_2=CHR^3, is introduced into the mixture and then block copolymers of general formula (I) are obtained:



According to this principle, the invention therefore also relates to a process for preparing multiblock polymers, in which the implementation of the process previously described is repeated at least once, using:

- different monomers from those of the previous implementation, and

- instead of the precursor compound of formula (II), the block polymer coming from the previous implementation.

If the implementation is repeated once, a triblock polymer will be obtained, if it is repeated

twice, a "quadriblock" polymer will be obtained, and so on. In this way, at each new implementation, the product obtained is a block polymer having an additional polymer block.

Therefore, in order to prepare multiblock polymers, the process consists in repeating, several times, the implementation of the preceding process on the block polymer coming from each previous implementation using different monomers.

According to this method of preparing multiblock polymers, when it is desired to obtain homogeneous block polymers without a composition gradient, and if all the successive polymerizations are carried out in the same reactor, it is essential for all the monomers used in one step to have been consumed before the polymerization of the next step starts, therefore before the new monomers are introduced.

The compounds of formula (IV) and (V) are particularly advantageous as they allow a polymer chain to be grown on at least two active sites. With this type of compound, it is possible to save on polymerization steps in order to obtain an n-block copolymer.

Thus, if p = 2 in the formula (IV) or (V), the first block is obtained by the polymerization of a monomer M1 in the presence of the compound of formula (IV) or (V). This first block may then grow at each of its ends by the polymerization of a second monomer M2.

A triblock copolymer is obtained, this triblock polymer can itself grow at each of its ends by the polymerization of a third monomer M3. Thus, a "pentablock" copolymer is obtained in only three steps.

If p is greater than 2, the process makes it possible to obtain homopolymers or block copolymers whose structure is "multi-branched" or "hyperbranched".

The polymerization may be carried out in bulk, in solution or in emulsion. Preferably, it is carried out in emulsion.

Preferably, the process is carried out semi-continuously.

The temperature may vary between ambient temperature and 150°C, depending on the nature of the monomers used.

In general, during the polymerization, the instantaneous polymer content with respect to the instantaneous amount of monomer and polymer is between 50 and 99% by weight, preferably between 75 and 99%, even more preferably between 90 and 99%. Polymer is understood to mean either the compound of formula (I) for synthesizing a block copolymer or the compound of formula (II) for synthesizing the precursor polymer. This content is maintained, in a known manner, by controlling the temperature, the rate of addition of the reactants and of the polymerization initiator.

The process according to the invention has the advantage of resulting in block polymers having a

low polydispersity index.

It also makes it possible to control the molecular mass of the polymers.

The invention therefore also relates to the block polymers which can be obtained by the above process.

In general, these polymers have a polydispersity index of at most 2, preferably of at most 1.5.

These results are especially obtained for block polymers of formula (I) which is chain-end functionalized by the alkyl xanthate group.

These polymers correspond to the polymers of general formula (I) for which Z^1 is a sulphur atom and Z^2 is an oxygen atom.

The preferred block polymers are those having at least two polymer blocks chosen from the following combinations:

- polystyrene/polymethyl acrylate
- polystyrene/polyethyl acrylate,
- polystyrene/poly(*tert*-butyl acrylate),
- polyethyl acrylate/polyvinyl acetate,
- polybutyl acrylate/polyvinyl acetate,
- polyethyl acrylate/poly(*tert*-butyl acrylate),
- poly(*tert*-butyl acrylate)/polyvinyl acetate,
- polyethyl acrylate/polybutyl acrylate,
- polybutyl acrylate/polyvinyl alcohol,
- polyacrylic acid/polyvinyl alcohol.

According to a preferred mode, the polymers have at least two polymer blocks chosen from the above combinations and are of general formula (I) in which:

- $Z^1 = S$, $Z^2 = O$, $R^1 = CHCH3(CO_2Et)$ and $R^2 = Et$, or
- $Z^1 = S$, $Z^2 = O$, $R^1 = CH(CO_2Et)_2$ and $R^2 = Et$.

Finally, the process for synthesizing the precursor polymers of general formula (II) also makes it possible to synthesize polymers having a low polydispersity index. In general, these precursor polymers have a polydispersity index of at most 2, preferably of at most 1.5, especially when these polymers are alkyl-xanthate functionalized polymers (Z^1 being a sulphur atom and Z^2 being an oxygen atom).

Preferably, n is greater than or equal to 6.

The compounds (II) particularly preferred are styrene ($Y' = H$, $Y = C_6H_5$, $b = 0$), methyl acrylate ($Y' = H$, $Y = COOMe$, $b = 0$), ethyl acrylate ($Y' = H$, $Y = COOEt$, $b = 0$), butyl acrylate ($Y' = H$, $Y = COOBu$, $b = 0$), tert-butyl acrylate ($Y' = H$, $Y = COOtBu$, $b = 0$), vinyl acetate ($Y' = H$, $Y = OCOMe$, $b = 0$) and acrylic acid ($Y' = H$, $Y = COOH$, $b = 0$) homopolymers, for which:

- $Z^1 = S$, $Z^2 = O$, $R^1 = CH(CH3)(CO_2Et)$ and $R^2 = Et$, or
- $Z^1 = S$, $Z^2 = O$, $R^1 = CH(CO_2Et)_2$ and $R^2 = Et$.

The following examples illustrate the invention without, however, limiting the scope thereof.

EXAMPLES

1. SYNTHESIS OF (alkyl xanthate) PRECURSORS OF FORMULA (III)

Example 1.1: Synthesis of the ethyl α-(O-ethylxanthyl)propionate precursor

Approximately 1 litre of ethanol and 80 ml of ethyl α-bromopropionate are introduced into a round-bottomed flask. The flask is immersed in an ice bath. Homogenization takes place with stirring and under a flow of nitrogen. When the temperature of the reaction mixture has stabilized, 109 g of potassium O-ethylxanthate are added. The stirring and nitrogen stream are maintained for approximately 4 hours during which the mixture becomes whitish because of the formation of KBr.

When the reaction has reached completion, approximately 1 litre of water is added to the reactor. The mixture becomes clear and yellow. The desired product is extracted from the water-alcohol phase by means of an ether/pentane (1/2) mixture and recovered by vacuum evaporation.

The ^{13}C NMR spectrum gives the following peaks: 171.21; 70.11; 61.62; 47.01; 16.82; 14.04; 13.60.

Example 1.2: Synthesis of the [1-(O-ethylxanthyl)ethyl]benzene precursor

1 litre of ethanol and 80 ml of (1-bromoethyl)benzene are introduced into a round-bottomed flask. The flask is immersed in an ice bath. Homogenization takes place with stirring and under a stream of nitrogen. When the temperature of the reaction mixture has stabilized, 104 g of potassium O-ethylxanthate are added. The stirring and stream of nitrogen are maintained for approximately 4 hours during which the medium becomes whitish because of the formation of KBr.

When the reaction has reached completion, approximately 1 litre of water is added to the reactor. The mixture becomes clear and yellow. The desired product is extracted from the water-alcohol phase by means of an ether/pentane (1/2) mixture and recovered by vacuum evaporation.

The ^{13}C NMR spectrum gives the following peaks: 213.25; 141.73; 128.57; 127.47; 126.49; 69.69; 49.21; 21.70; 13.71.

Example 1.3: Synthesis of the α,α'-di(O-ethylxanthyl)-p-xylene precursor

Approximately 1 litre of ethanol and 80 ml of α,α'-dichloro-p-xylene are introduced into a round-bottomed flask. The flask is immersed in an ice bath. Homogenization takes place with stirring and under a stream of nitrogen. When the temperature of the reaction medium has stabilized, 184 g of potassium

O-ethylxanthate are added. The stirring and stream of nitrogen are maintained for approximately 4 hours during which the medium becomes whitish because of the formation of KCl.

When the reaction has reached completion, approximately 1 litre of water is added to the reactor. The mixture becomes clear and yellow. The desired product is extracted from the water-alcohol phase by means of a dichloromethane/ether/pentane (1/1/2) mixture and recovered by vacuum evaporation.

The ^{13}C NMR spectrum gives the following peaks: 135.27; 129.42; 70.23; 40.12; 13.89.

Example 1.4: Synthesis of the α-(O-ethylxanthyl)-α-phthalimidoacetophenone precursor

74 ml of acetone and 12.7 g of α-bromo-α-phthalimidoacetophenone are introduced into a round-bottomed flask. The mixture is homogenized with stirring and under a stream of nitrogen. 6.5 g of potassium O-ethylxanthate salt are added. The reaction lasts 5 min, after which the reaction mixture is diluted with distilled water.

The precipitated solid is filtered, dried and purified by recrystallization in ethanol.

The ^{13}C NMR spectrum gives the following peaks: 210.0; 189.2; 166.2; 134.4; 133.8; 133.6; 131.5; 128.7; 128.4; 123.7; 71.6; 61.8; 13.6.

Example 1.5: Synthesis of the ethyl α-(O-ethylxanthyl)-α-phenylthiopropionate precursor

11 ml of acetone and 2.36 g of potassium O-ethylxanthate salt are introduced into a round-bottomed flask. The mixture is homogenized with stirring and under a stream of nitrogen, and then a solution of ethyl α-chloro-α-phenolthiopropionate (1.56 g) in acetone (4 ml) is added drop by drop. The mixture is stirred for 30 min. The solvent is evaporated. The residue [lacuna] diluted with ether and then washed in water.

The organic phase is separated and dried on sodium sulphate. The product is recovered after concentration in vacuo and purification by chromatography on silica.

The ^{13}C NMR spectrum gives the following peaks: 211.3; 168.8; 137.6; 130.4; 129.0; 128.9; 69.72; 62.99; 62.13; 25.56; 13.80; 13.37.

Example 1.6: Synthesis of the (O-ethylxanthyl)malonate precursor

50 ml of acetone and 4 ml of diethylchloromalonate are introduced into a round-bottomed flask. The mixture is homogenized with stirring and under a stream of nitrogen and 4.4 g of potassium O-ethylxanthate salt is added. The reaction lasts 1 hour, after which the reaction medium is diluted with 20 ml of water.

The product is extracted from the phase thus obtained by 50 ml of ether, and then purified by flash chromatography.

The ^{13}C NMR spectrum gives the following peaks: 210.3; 165.2; 71.0; 62.8; 56.4; 14.0; 13.6.

Example 1.7: Synthesis of the ethyl α-(O-phenylethylxanthyl)-α-phenylthiopropionate precursor

20 ml of acetone and 5.58 g of potassium O-phenylethylxanthate are introduced into a round-bottomed flask. The mixture is homogenized with stirring and under a stream of nitrogen, then the temperature is lowered to 0°C.

A solution of ethyl α-chloro-α-phenylthiopropionate (6.15 g) in acetone (20 ml) is added to the flask drop by drop. The mixture is stirred for 2 hours.

Next, the solvent is evaporated. The residue is diluted with ether, washed firstly with water and then with a saturated aqueous solution of NaCl. The organic phase is separated and dried on sodium sulphate.

The product is recovered in the form of white crystals after evaporation and recrystallization in ether at room temperature.

The ^{13}C NMR spectrum gives the following peaks: 211.27; 168.82; 130.42; 69.72; 62.13; 25.56;

13.80; 13.37.

Example 1.8: Synthesis of the ethyl α-(O-phenylethylxanthyl)-α-phenylethanoate precursor

1 equivalent of phenylethyl alcohol (16.78 ml) in solution in 150 ml of THF is introduced into a round-bottomed flask after which is added 1 equivalent of NaH (5.68 g) at 0°C.

After 2 hours of stirring, 1 equivalent of CS_2 (8.48 ml) is added.

After stirring overnight at room temperature, the solution is filtered. The salt is washed with pentane and then dried. It is isolated quantitatively in the form of a yellow powder, 1.09 g of which are dissolved in 5 ml of acetone. The solution is cooled to 0°C.

1 equivalent (0.99 g) of ethyl α-chlorophenylethanoate is added. The solution is stirred for 3 hours at room temperature.

Next, it is extracted with ether, dried on magnesium sulphate and concentrated in vacuo.

1.62 g of ethyl α-(O-phenylethylxanthyl)-α-phenylethanoate is recovered. The overall reaction yield is 90%.

Example 1.9: Synthesis of the (O-ethylxanthyl)isobutyronitrile precursor

10 ml of bis(O-ethyl)xanthate (2.42 g) is dissolved in 36 ml of hexane in a 100 ml round-bottomed flask provided with a refrigerant and under an inert atmosphere of argon.

The solution is heated for 15 min and then 1 equivalent of azobis(isobutyronitrile) (AIBN) (1.64 g) is added. 0.5 equivalent of AIBN (0.82 g) is added after two and a half hours.

The solution is dried under vacuum. The product is purified by chromatography and isolated. The yield is 77%.

Example 1.10: Synthesis of the ethyl (O-neopentylxanthyl)malonate precursor

1 equivalent of neopentyl alcohol (2.15 ml) in solution in 30 ml of THF is introduced into a round-bottomed flask. 1 equivalent of NaH (0.81 g) is then added at 0°C.

After two hours of stirring, 1 equivalent of CS_2 (1.21 ml) is added.

After stirring overnight at room temperature, the solution is filtered. The salt is washed with pentane and then dried. It is isolated quantitatively in the form of a yellow powder, 1.86 g of which is dissolved in 10 ml of acetone. The solution is cooled to 0°C.

1 equivalent of ethylchloromalonate (1.61 ml) in 5 ml of acetone is added. The solution is stirred

for 4 hours at room temperature. It is then hydrolysed and extracted with ether. It is then dried on magnesium sulphate and concentrated in vacuo.

After purification by chromatography, 2.08 g of product is isolated. The yield is 65%.

Example 1.11: Synthesis of the ethyl (O-isobornylxanthyl)malonate precursor

15.4 g of isoborneol in solution in 200 ml of THF are introduced into a round-bottomed flask. The solution is treated with 1 equivalent of NaH at 0°C then, after 2 hours of stirring, 6 ml of CS_2 are added.

The solution is stirred overnight at room temperature and then filtered. The salts are then washed with ether. The filtrate is concentrated. It is taken up in pentane and filtered. Finally, it is dried in order to obtain the sodium salt quantitatively.

5.04 g of this salt are dissolved in 40 ml of acetone. The solution is cooled to 0°C. 3.08 ml of ethylchloromalonate are added. The solution is stirred for one hour at 0°C. Next, it is hydrolysed, extracted with ether and then dried on magnesium sulphate and concentrated in vacuo.

After purification by chromatography on silica, 5.92 g of product are obtained. The yield is 80%.

Example 1.12: Synthesis of the (O-isopropylxanthyl)valeronitrile precursor

0.336 g of azobisvaleronitrile and 0.27 g of bis(O-isopropyl)xanthate are dissolved in dioxane. The temperature is raised to 101°C.

After 12 hours of stirring, the solvent is evaporated and the residue purified by chromatography on silica.

The product is obtained with a 60% yield.

EXAMPLES 2 - SYNTHESIS OF THE PRECURSORS OF FORMULA (II) (homopolymers)

Example 2.1: Styrene homopolymer

1 mmol of ethyl α-(O-ethylxanthyl)propionate (0.222 g) and 40 mmol of styrene (4.16 g) are introduced into a 10 ml round-bottomed flask. The temperature is raised to 125°C and 0.03 mmol of lauroyl peroxide (12.8 mg) are added.

The polymerization lasts 9 hours, after which several additions of initiator are made:

- 0.02 mmol after two hours,
- 0.02 mmol after four hours,
- 0.01 mmol after six hours,
- 0.01 mmol after eight hours.

The polymer is recovered by precipitation in methanol and analysed by GPC in a THF medium and in polystyrene equivalents (see Table 9).

Example 2.2: Styrene homopolymer

1 mmol of [1-(O-ethylxanthyl)ethyl]benzene (0.226 g) and 40 mmol of styrene (4.16 g) are introduced into a 10 ml round-bottomed flask. The temperature is raised to 90°C and 0.02 mmol of lauroyl peroxide (8.52 mg) are added.

The polymerization lasts 12 hours, during which several additions of initiator are made:

- 0.01 mmol after two hours,
- 0.01 mmol after four hours,
- 0.01 mmol after six hours,
- 0.01 mmol after eight hours,
- 0.01 mmol after ten hours.

The polymer is recovered by precipitation in methanol and analysed by GPC in a THF medium and in polystyrene equivalents (see Table 9).

Example 2.3: Styrene homopolymer

1 mmol of α,α'-di(O-ethylxanthyl)-p-xylene (0.346 g) and 40 mmol of styrene (4.16 g) are introduced into a 10 ml round-bottomed flask. The temperature is raised to 90°C and 0.02 mmol of lauroyl peroxide (8.52 mg) are added.

The polymerization lasts 15 hours, during which several additions of initiator are made:

- 0.01 mmol after two hours,
- 0.01 mmol after four hours,
- 0.01 mmol after six hours,

- 0.01 mmol after eight hours,
- 0.01 mmol after twelve hours,
- 0.01 mmol after fourteen hours.

The polymer is recovered by precipitation in methanol and analysed by GPC in a THF medium and in polystyrene equivalents (see Table 9).

Example 2.4: Styrene homopolymer

1 mmol of α-(O-ethylxanthyl)-α-phthalimidoacetophenone (0.385 g) and 40 mmol of styrene (4.16 g) are introduced into a 10 ml round-bottomed flask. The temperature is raised to 90°C and 0.02 mmol of lauroyl peroxide (8.52 mg) are added.

The polymerization lasts 15 hours, during which several additions of initiator are made:

- 0.01 mmol after two hours,
- 0.01 mmol after four hours,
- 0.01 mmol after six hours,
- 0.01 mmol after eight hours,
- 0.01 mmol after twelve hours,
- 0.01 mmol after fourteen hours.

The polymer is recovered by precipitation in methanol and analysed by GPC in a THF medium and in polystyrene equivalents (see Table 9).

Example 2.5: Styrene homopolymer

1 mmol of ethyl α-(O-ethylxanthyl)-α-phenylthiopropionate (0.33 g) and 40 mmol of styrene

(4.16 g) are introduced into a 10 ml round-bottomed flask. The temperature is raised to 90°C and 0.02 mmol of lauroyl peroxide (8.52 mg) are added.

The polymerization lasts 15 hours, during which several additions of initiator are made:

- 0.01 mmol after two hours,
- 0.01 mmol after four hours,
- 0.01 mmol after six hours,
- 0.01 mmol after eight hours,
- 0.01 mmol after twelve hours,
- 0.01 mmol after fourteen hours.

The polymer is recovered by precipitation in methanol and analysed by GPC in a THF medium and in polystyrene equivalents (see Table 9).

Example 2.6: Methyl acrylate homopolymer

1 mmol of ethyl α-(O-ethylxanthyl)propionate (0.222 g), 40 mmol of methyl acrylate (MeA) (3.44 g) and 3.5 ml of toluene are introduced into a 10 ml round-bottomed flask. The temperature is raised to 100°C and 0.035 mmol of lauroyl peroxide (14.9 mg) are added. The polymerization lasts 15 hours, during which several additions of initiator are made:

- 0.02 mmol after two hours,
- 0.02 mmol after six hours,
- 0.02 mmol after ten hours.

The polymer is recovered by evaporating, under high vacuum, the solvent and the traces of

residual monomers and is analysed by GPC in THF medium and polystyrene equivalents (see Table 9).

Example 2.7: Methyl acrylate homopolymer

1 mmol of ethyl α-(O-ethylxanthyl)propionate (0.222 g) and 40 mmol of methyl acrylate (3.44 g) are introduced into a 10 ml round-bottomed flask. The temperature is raised to 80°C and 0.03 mmol of lauroyl peroxide (12.8 mg) are added.

The polymerization lasts 45 min.

The polymer is recovered by evaporating, under high vacuum, the solvent and the traces of residual monomers. It is analysed by GPC in THF medium and in polystyrene equivalents (see Table 9).

Example 2.8: Methyl acrylate homopolymer

1 mmol of ethyl α-(O-ethylxanthyl)propionate (0.222 g) and 80 mmol of methyl acrylate (6.88 g) are introduced into a 10 ml round-bottomed flask. The temperature is raised to 80°C and 0.02 mmol of lauroyl peroxide (8.52 mg) are added. The polymerization lasts 45 min.

The polymer is recovered by evaporating, under high vacuum, the traces of residual monomers. It is analysed by GPC in THF medium and in polystyrene equivalents (see Table 9).

Example 2.9: Methyl acrylate homopolymer

1 mmol of α-(O-ethylxanthyl)-α-phthalimidoacetophenone (0.385 g) and 40 mmol of methyl acrylate (3.44 g) are introduced into a 10 ml round-bottomed flask. The temperature is raised to 80°C and 0.02 mmol of lauroyl peroxide (8.52 mg) are added. The polymerization lasts 45 min.

The polymer is recovered by evaporating, under high vacuum, the traces of residual monomers. It is analysed by GPC (see Table 9).

Example 2.10: Ethyl acrylate homopolymer

1 mmol of ethyl α-(O-ethylxanthyl)propionate (0.222 g) and 40 mmol of ethyl acrylate (EtA) (3.44 g) are introduced into a 10 ml round-bottomed flask. The temperature is raised to 80°C and 0.02 mmol of lauroyl peroxide (8.52 mg) are added. The polymerization lasts 6 hours.

The polymer is recovered by evaporating, under high vacuum, the traces of residual monomers. It is analysed by GPC in THF medium and in polystyrene equivalents (see Table 9).

Example 2.11: Methyl acrylate homopolymer

1 mmol of ethyl α-(O-ethylxanthyl)-α-phenylthiopropionate (0.33 g) and 40 mmol of methyl acrylate (3.44 g) are introduced into a 10 ml round-bottomed flask. The temperature is raised to 80°C and

0.02 mmol of lauroyl peroxide (8.52 mg) are added.

The polymerization lasts 6 hours.

The polymer is recovered by evaporating, under high vacuum, the traces of residual monomers. It is analysed by GPC in THF medium and in polystyrene equivalents (see Table 9).

Example 2.12: 2-ethylhexyl acrylate homopolymer

1 mmol of (O-ethylxanthyl)malonate (0.28 g) and 40 mmol of 2-ethylhexyl acrylate (2EHA) (7.36 g) are introduced into a 10 ml round-bottomed flask. The temperature is raised to 80°C and 0.02 mmol of lauroyl peroxide (8.52 mg) are added.

The polymerization lasts 6 hours.

The polymer is recovered by evaporating, under high vacuum, the traces of residual monomers. It is analysed by GPC in THF medium and in polystyrene equivalents (see Table 9).

Example 2.13: Vinyl acetate homopolymer

1 mmol of ethyl α-(O-ethylxanthyl)propionate (0.222 g) and 40 mmol of vinyl acetate (MVA) (3.44 g) are introduced into a 10 ml round-bottomed flask. The temperature is raised to 80°C and 0.02 mmol of lauroyl peroxide (8.52 mg) are added.

The polymerization lasts 8 hours, during which several additions of initiator are made:

- 0.01 mmol after two hours,
- 0.01 mmol after four hours,
- 0.01 mmol after six hours.

The polymer is recovered by evaporating, under high vacuum, the traces of residual monomers and analysed by GPC in THF medium and in polystyrene equivalents (see Table 9).

Example 2.14: Vinyl acetate homopolymer

1 mmol of ethyl α-(O-ethylxanthyl)propionate (0.222 g) and 40 mmol of vinyl acetate (3.44 g) are introduced into a 10 ml round-bottomed flask. The temperature is raised to 80°C and 0.02 mmol of lauroyl peroxide (8.52 mg) are added.

The polymerization lasts 4 hours.

The polymer is recovered by evaporating, under high vacuum, the traces of residual monomers. It is analysed by GPC in THF medium and in polystyrene equivalents (see Table 9).

Example 2.15: Styrene homopolymer

1 mmol (3.8 g) of the polymer from Example 2.1, chain-end functionalized by the O-ethylxanthyl group, and 40 mmol of styrene (4.16 g) are introduced into a 10 ml round-bottomed flask. The temperature is raised to 90°C and 0.02 mmol of lauroyl peroxide (8.52 mg) are added. The polymerization lasts 10 hours, during which several additions of initiator are made:

- 0.01 mmol after two hours,
- 0.01 mmol after four hours,
- 0.01 mmol after six hours,
- 0.01 mmol after eight hours.

The polymer is recovered by precipitation in methanol and analysed by GPC in THF medium and in polystyrene equivalents (see Table 9).

This polymer is a styrene homopolymer, but it was obtained as a diblock copolymer with two polystyrene blocks.

Example 2.16: Styrene homopolymer

The following are introduced into a 2 l reactor:

- 0.4 g of sodium bicarbonate,
- 5.4 g of sodium laury sulphate, and
- 1020 g of water.

The temperature is increased to 85°C.

An aqueous ammonium persulphate solution (1.6 g of water + 0.8 g of ammonium persulphate) is added.

A mixture containing 400 g of styrene and 2.22 g of ethyl α-(O-ethylxanthyl)propionate is added continuously over a period of 2 hours.

The temperature is maintained at 85°C for an additional 1 hour, during which an aqueous ammonium persulphate solution (0.8 g of water + 0.4 g of ammonium persulphate) is introduced.

The polymer obtained is recovered after coagulation of the emulsion and analysed by GPC in THF medium and in polystyrene equivalents (see Table 9).

Example 2.17: Styrene homopolymer

1 mmol of (O-ethylxanthyl)malonate (0.28 g) and 40 mmol of styrene (4.16 g) are introduced into a 10 ml round-bottomed flask. The temperature is raised to 95°C and 0.03 mmol of lauroyl peroxide (12.8 mg) are added.

The polymerization lasts 10 hours, during which several additions of initiator are made:

- 0.02 mmol after two hours,
- 0.02 mmol after four hours,
- 0.02 mmol after six hours,
- 0.02 mmol after eight hours.

The polymer is recovered by precipitation in methanol.

It is analysed by GPC in THF medium and in polystyrene equivalents (see Table 9).

Example 2.18: Methyl acrylate homopolymer

1 mmol of (O-ethylxanthyl)malonate (0.28 g) and 40 mmol of methyl acrylate (3.44 g) are introduced into a 10 ml round-bottomed flask containing 4 ml of toluene. The temperature is raised to 80°C and 0.03 mmol of lauroyl peroxide (12.8 mg) are added.

The polymerization lasts 26 hours, during

which 0.02 mmol of lauroyl peroxide are added every two hours.

The polymer is recovered by evaporating, under high vacuum, the toluene and the traces of residual monomer.

It is analysed by GPC in THF medium and in polystyrene equivalents (see Table 9).

Example 2.19: Styrene homopolymer

1 mmol of ethyl α-(O-phenylethyl)-α-phenylthiopropionate (0.406 g) and 40 mmol of styrene (4.16 g) are introduced into a 10 ml round-bottomed flask. The temperature is raised to 95°C and 0.03 mmol of lauroyl peroxide (12.8 mg) are added.

The polymerization lasts 16 hours, during which 0.02 mmol of lauroyl peroxide are added every two hours.

The polymer is recovered by precipitation in methanol.

It is analysed by GPC in THF medium and in polystyrene equivalents (see Table 9).

Example 2.20: Methyl acrylate homopolymer

1 mmol of ethyl α-(O-phenylethylxanthyl)-α-phenylethanoate (0.36 g) and 40 mmol of methyl acrylate (3.44 g) are introduced into a 10 ml round-bottomed flask. The temperature is raised to 80°C and 0.03 mmol of lauroyl peroxide (12.8 mg) are added.

The polymerization lasts 11 hours, during which 0.02 mmol of lauroyl peroxide are added every two hours.

The polymer is recovered by evaporating, under high vacuum, the traces of residual monomer.

It is analysed by GPC in THF medium and in polystyrene equivalents (see Table 9).

Example 2.21: Methyl acrylate homopolymer

1 mmol of (O-ethylxanthyl)isobutyronitrile (0.189 g) and 40 mmol of methyl acrylate (3.44 g) are introduced into a 10 ml round-bottomed flask. The temperature is raised to 80°C and 0.03 mmol of lauroyl peroxide (12.8 mg) are added.

The polymerization lasts 6 hours, during which 0.02 mmol of lauroyl peroxide are added every two hours, after 2 and 4 hours.

The polymer is recovered by evaporating, under high vacuum, the traces of residual monomers.

It is analysed by GPC in THF medium and in polystyrene equivalents (see Table 9).

Example 2.22: Methyl acrylate homopolymer

1 mmol of ethyl (O-neopentylxanthyl)malonate (0.322 g) and 40 mmol of methyl acrylate (3.44 g) are introduced into a 10 ml round-bottomed flask. The temperature is raised to 80°C and 0.03 mmol of lauroyl peroxide (12.8 mg) are added.

The polymerization lasts 4 hours, during which 0.02 mmol of lauroyl peroxide are added after two hours.

The polymer is recovered by evaporating, under high vacuum, the traces of residual monomer.

It is analysed by GPC in THF medium and in polystyrene equivalents (see Table 9).

Example 2.23: Methyl acrylate homopolymer

1 mmol of ethyl (O-isobornylxanthyl)malonate (0.388 g) and 40 mmol of methyl acrylate (3.44 g) are added to a 10 ml round-bottomed flask. The temperature is raised to 80°C and 0.03 mmol of lauroyl peroxide (12.8 mg) are added.

The polymerization lasts 2 hours 30 minutes during which 0.02 mmol of lauroyl peroxide are added after 2 hours.

The polymer is recovered by evaporating, under high vacuum, the traces of residual monomer.

It is analysed by GPC in THF medium and in polystyrene equivalents (see Table 9).

Example 2.24: Vinyl acetate homopolymer

1 mmol of ethyl (O-isobornyl)malonate (0.388 g) and 77 mmol of vinyl acetate (6.62 g) are introduced into a 10 ml round-bottomed flask. The temperature is raised to 70°C and 0.01 mmol of AIBN (azobisisobutyronitrile) (1.64 mg) are added. The

polymerization lasts 24 hours, during which several additions of AIBN are made:

- 1.4 mg after two hours,
- 2.2 mg after four hours.

The polymer is recovered by evaporating, under high vacuum, the traces of residual monomers.

It is analysed by GPC in THF medium and in polystyrene equivalents (see Table 9).

Example 2.25: Acrylic acid homopolymers

25 g of acrylic acid are dissolved in 85 g of water and then the solution thus obtained is neutralized to a pH between 6 and 7: this solution is solution 1.

0.35 g of 2,2′-azobis(2-methylpropionamide)-dihydrochloride are dissolved in 150 g of water: this solution is solution 2.

Into three round-bottomed flasks, each containing a different quantity of (O-isopropylxanthyl)-valeronitrile, are introduced 11 g of solution 1 and 1.5 g of solution 2. The compositions of the various flasks are shown in Table A.

The temperature is raised to 70°C and polymerization is carried out over 24 hours.

The polymer is recovered by evaporating, under high vacuum, the water and the traces of residual monomer.

It is analysed by GPC in aqueous medium and

in PEO equivalents, the results being given in Table 1.

Table 1

Mass of precursor (g)	Degree of conversion (%)	M_n	PI
0.065	100	14,800	1.7
0.108	100	12,000	1.4
0.163	100	8,900	1.4

Example 2.26: Acrylic acid homopolymer

1 mmol of ethyl α-(O-ethylxanthyl)propionate (0.222 g) and 40 mmol of acrylic acid (2.88 g) are introduced into a 10 ml round-bottomed flask. The temperature is raised to 80°C and 0.04 mmol of lauroyl peroxide (17 mg) are added.

The polymerization lasts 6 hours, during which several additions of lauroyl peroxide are made:

- 0.04 mmol after two hours,
- 0.04 mmol after four hours.

The polymer is recovered by evaporating, under high vacuum, the traces of residual monomer.

It is analysed by GPC in aqueous medium and in PEO equivalents (see Table 9).

Example 2.27: Acrylic acid homopolymers

Several acrylic acid homopolymers are prepared in the following manner.

All the acrylic acid (AA), the AIBN and the ethyl α-(O-ethylxanthyl)propionate precursor are mixed together and introduced into a round-bottomed flask. The amounts are given in Table 2. The temperature is raised to 80°C.

The polymerization lasts 6 hours.

The traces of residual monomer are removed by evaporation.

The results, obtained from GPC analysis in THF medium and in polystyrene equivalents, are given in Table 2.

Table 2

AA mass (g)	AIBN mass (mg)	Precursor mass (g)	M_n	PI
1.53	3.47	0.35	345	1.12
3.39	1.81	0.2	770	1.10
3.85	1.15	0.13	1060	1.25
4.08	0.92	0.10	1290	1.30

Example 2.28: Acrylic acid homopolymers

Several acrylic acid homopolymers are prepared in solution in the following manner.

All the acrylic acid (AA), the AIBN and the ethyl α-(O-ethylxanthyl)propionate precursor are dissolved in acetone in a round-bottomed flask. The respective amounts of each ingredient are given in Table 3.

The temperature is raised to 60°C.

The polymerization lasts 3 hours.

The traces of residual monomer and the solvent are removed by evaporation.

The results, obtained by GPC analysis in THF medium and in polystyrene equivalents, are given in Table 3.

Table 3

AA mass (g)	AIBN mass (mg)	Precursor mass (g)	Volume of solvent (ml)	M_n	PI
5.07	2.93	0.3	8	550	1.10
3.88	1.12	0.12	5	1170	1.19
4.37	0.63	0.07	5	1760	1.29
4.56	0.44	0.05	5	1920	1.27

Example 2.29: Ethyl acrylate homopolymer

The following are introduced into a round-bottomed flask:

- 33.2 mg of ethyl α-(O-ethylxanthyl)propionate (1 equivalent),
- 5.01 g of ethyl acrylate (160 equivalents), and
- 8.2 mg of AIBN.

The temperature is raised to 70°C. The polymerization lasts 24 hours.

The polymer is recovered by evaporating, under high vacuum, the traces of residual monomer.

It is analysed by GPC in THF medium and in polystyrene equivalents (see Table 9).

Example 2.30: Vinyl acetate homopolymer

4.3 g of vinyl acetate and 59.7 mg of lauroyl peroxide are introduced into three round-bottomed flasks containing varying amounts of ethyl α-(O-ethylxanthyl)propionate. The temperature is raised to 70°C and the polymerization lasts 6 hours. The amounts of precursor used are given in Table 4.

The polymer is recovered by evaporating, under high vacuum, the traces of residual monomer. The results, obtained by GPC analysis in THF medium and in polystyrene equivalents, are given in Table 4.

Table 4

Mass of precursor (g)	Degree of conversion (%)	M_n	PI
0.266	64.4	2100	1.4
0.130	66.6	4100	1.6
0.068	66.0	7000	1.9

Example 2.31: Styrene homopolymer obtained in emulsion

The following are introduced into a 1.5 l reactor fitted with a Teflon anchor stirrer:

- 525 g of water,
- 0.2 g of sodium hydrogen carbonate and
- 10 g of sodium lauryl sulphate.

The temperature is raised to 70°C and 20 g of styrene and all of the ethyl α-(O-ethylxanthyl)propionate precursor are added in one go.

Next, the temperature is increased to 85°C and 0.4 g of ammonium persulphate in solution in 16.13 g of water are added in one go.

Styrene (180 g) is then continuously fed in over a period of four hours.

The temperature is maintained at 85°C for an additional 2 hours.

The results, obtained from GPC analysis in

THF medium and in polystyrene equivalents, are given in Table 5.

Table 5

Mass of precursor (g)	Degree of conversion (%)	M_n	PI
2	88	15,400	1.9
1	90	29,500	1.9

Example 2.32: Styrene homopolymer obtained in emulsion

The following are introduced into a 1.5 l reactor fitted with a Teflon anchor stirrer:

- 475 g of water,
- 0.2 g of sodium hydrogencarbonate and
- 10 g of sodium lauryl sulphate.

The temperature is raised to 70°C and the following are added in one go:

- 20 g of styrene and
- 2 g of ethyl α-(O-ethylxanthyl)propionate.

Next, the temperature is increased to 85°C and 0.4 g of ammonium persulphate in solution in 16.13 g of water are added in one go.

The following are introduced into the reactor, continuously and simultaneously:

- 180 g of styrene over 8 hours,

- 0.4 g of ammonium persulphate in 50.4 g of water over 10 hours.

Specimens are removed regularly and analysed by GPC in THF medium and in polystyrene equivalents. The results obtained are given in Table 6.

Table 6

Time (h)	Degree of conversion (%)	M_n	PI
1	10.1	2500	1.8
2	18.6	3300	1.8
4	39.2	6250	1.9
6	56.3	8100	1.9
8	73.3	10,000	1.9
24	75.7	10,500	1.9

A linear increase in the molecular masses with conversion is observed, thereby demonstrating the controlled character of the radical polymerization.

Example 2.33: Ethyl acrylate homopolymer

A solution is prepared which contains:

- 17.64 g of ethyl acrylate;
- 0.459 g of ethyl α-(O-ethylxanthyl)propionate and
- 0.036 g of AIBN.

1 g of this solution is introduced into 7

tubes which will serve to determine the polymerization kinetics.

These tubes are then heated to 70°C and stopped at different times. For each tube, the polymer is recovered by evaporating the traces of residual monomer and analysed by GPC in THF medium and in polystyrene equivalents.

The results obtained are given in Table 7.

Table 7

Time (min)	Degree of conversion (%)	M_n	PI
12	0	1900	3.4
21	17	4200	2.5
30	32.3	4300	2.5
42	43.5	4800	2.4
53	46.6	4800	2.5
66	71.4	6700	1.9
124	80.4	7100	1.9

A linear increase in the molecular masses with conversion is observed, thereby demonstrating the controlled character of the radical polymerization.

Example 2.34: Vinyl acetate homopolymer

A solution is prepared which contains:

- 7.35 g of vinyl acetate,
- 0.229 g of ethyl α-(O-ethylxanthyl)propionate, and
- 0.018 g of AIBN.

1 g of this solution is introduced into 4 tubes which will serve to determine the polymerization kinetics.

The tubes are then heated to 70°C and stopped at different times. For each tube, the polymer is recovered by evaporating the traces of residual monomer and analysed by GPC in THF medium and in polystyrene equivalents.

The results obtained are given in Table 8.

Table 8

Time (min)	Degree of conversion (%)	M_n	PI
12	0		
28	13.8	1200	1.4
38	77.8	4300	1.7
51	83.9	4300	1.7

A linear increase in the molecular masses with conversion is observed, thereby demonstrating the controlled character of the radical polymerization.

Results of Examples 2.1 to 2.24, 2.26 and 2.29:

GPC analysis of the homopolymers obtained above is used to measure their number-average mass (M_n). It is also used to measure their weight-average mass (M_w) and hence their polydispersity index (PI) corresponding to the ratio of M_w to M_n.

GPC chromatograms are systematically produced in double detection mode, namely refractometry (RI) and UV absorption (UV). The UV detection wavelength corresponds to the maximum absorption of the xanthate functional group fixed on the end of the chain according to the formula claimed. For all the specimens analysed, there is perfect superposition of the chromatograms obtained from one or other detection mode. This result indicates that the chain ends are functionalized and constitutes an additional proof of the assumed structure of the polymers according to the invention.

Table 9

Examples	Monomer	M_n	PI	Degree of conversion
Ex. 2.1	styrene	3800	2	
Ex. 2.2	styrene	5200	2.1	
Ex. 2.3	styrene	7900	2.5	
Ex. 2.4	styrene	3200	1.8	
Ex. 2.5	styrene	3300	1.9	
Ex. 2.6	MeA	3500	1.8	
Ex. 2.7	MeA	3750	1.7	
Ex. 2.8	MeA	7300	1.7	
Ex. 2.9	MeA	3000	1.4	
Ex. 2.10	EtA	3700	1.6	
Ex. 2.11	MeA	3500	1.35	
Ex. 2.12	2EHA	6900	1.5	
Ex. 2.13	MVA	3200	1.35	
Ex. 2.14	MVA	2100	1.18	
Ex. 2.15	styrene	6200	2	
Ex. 2.16	styrene	3800	1.6	
Ex. 2.17	styrene	4300	1.9	78
Ex. 2.18	MeA	3900	1.5	95
Ex. 2.19	styrene	3400	1.8	77
Ex. 2.20	MeA	3100	1.6	60
Ex. 2.21	MeA	3600	1.4	75
Ex. 2.22	MeA	5100	1.4	90
Ex. 2.23	MeA	4000	1.7	88
Ex. 2.24	MVA ?	2500	1.8	29
Ex. 2.26	AA	6600	2.3	97
Ex. 2.29	EtA	29,400	1.9	93

Example 2.35: Vinyl acetate homopolymer

The following are introduced into a 10 ml round-bottomed flask:

- 0.899 g of vinyl acetate (i.e. approximately 10 equivalents),
- 0.220 g of ethyl α-(O-ethylxanthylpropionate (1 equivalent), and
- 17.2 mg of AIBN.

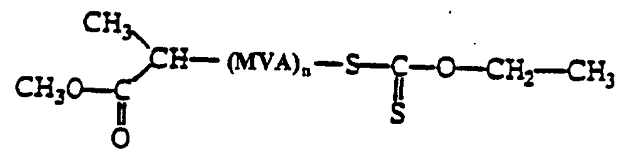
The temperature is raised to 70°C. The polymerization lasts 24 hours.

The polymer is recovered by evaporating, under high vacuum, the traces of residual monomer and is analysed by MALDI-TOF on a DHB matrix. The results are given in Table 10.

Table 10

Number of MVA units	Theoretical mass (g)	MALDI-TOF mass (g)
7	833	831.556
8	919	917.458
9	1005	1003.638

In Table 10, the theoretical masses are calculated assuming a structure according to the formula:



It is necessary to add 23 g to the mass obtained since the species detected are in sodium salt form. The excellent agreement between the theoretical masses and the masses measured by MALDI-TOF confirm the assumed mechanism for the polymerization and the structure of the polymers obtained.

<u>EXAMPLES 3 - SYNTHESES OF BLOCK COPOLYMERS</u>

Example 3.1: p(MeA-b-St) block copolymer

The following are introduced into a 10 ml round-bottomed flask:

- 1 mmol of ethyl α-(O-ethylxanthyl)propionate (0.222 g) and
- 20 mmol of methyl acrylate (1.72 g).

The mixture is heated to 80°C and 0.02 mmol of lauroyl peroxide (8.52 mg) are added. The mixture is maintained at temperature for 45 min after which it coagulates. Next, the reaction mixture is dissolved in 3 ml of toluene and then evaporated to dryness, in vacuo. This operation is repeated three times in order to remove the traces of residual methyl acrylate. This synthesis results in a precursor which can be used for preparing a block copolymer.

Next, 20 mmol of styrene (2.08 g) are introduced into the reactor. The temperature is raised to 110°C and 0.02 mmol of lauroyl peroxide (8.52 mg) are added. This second step lasts 6 hours, during which several additions of initiator are made:

- 0.01 mmol after two hours,
- 0.01 mmol after four hours.

The copolymer obtained is recovered by precipitation in methanol and analysed by double detection GPC - refractometry and UV spectrometry. The GPC solvent is THF and the masses are given in polystyrene equivalents. The results are given in Table 12.

Example 3.2: p(St-b-MeA) block copolymer

The following are introduced into a 10 ml round-bottomed flask:

- 1 mmol of ethyl α-(O-ethylxanthyl)propionate (0.222 g),
- 20 mmol of styrene (2.08 g), and
- 1 ml of toluene.

The reaction mixture is raised to 110°C and 0.025 mmol of lauroyl peroxide (10.6 mg) are introduced into the reactor. This first step lasts 9 hours, during which several additions of initiator are made:

- 0.01 mmol after two hours,
- 0.01 mmol after four hours,
- 0.01 mmol after six hours,

- 0.01 mmol after eight hours.

Next, the mixture is cooled to 80°C and the following are introduced:

- 20 mmol of methyl acrylate (1.72 g) and
- 0.03 mmol of lauroyl peroxide (12.8 mg).

This second step lasts 7 hours, during which several additions of initiator are made:

- 0.01 mmol after two hours,
- 0.01 mmol after four hours,
- 0.01 mmol after six hours.

The polymer obtained is recovered and analysed as in Example 3.1. The results are given in Table 11.

Example 3.3: p(St-b-MeA) block copolymer

The following are introduced into a 10 ml round-bottomed flask:

- 1 mmol of [1-(O-ethylxanthyl)ethyl]benzene (0.226 g) and
- 20 mmol of styrene (2.08 g).

The temperature is raised to 90°C and 0.03 mmol of lauroyl peroxide (12.8 mg) are added. The temperature is maintained at 90°C for 10 hours, during which several additions of initiator are made:

- 0.01 mmol after two hours,
- 0.01 mmol after four hours,
- 0.01 mmol after six hours,
- 0.01 mmol after eight hours.

Next, the reaction mixture is cooled to 80°C and the following are introduced:

- 20 mmol of methyl acrylate (1.72 g) and
- 0.02 mmol of lauroyl peroxide (8.52 mg).

This second step lasts 8 hours, during which several additions of initiator are made:

- 0.01 mmol after two hours,
- 0.01 mmol after four hours,
- 0.01 mmol after six hours,
- 0.01 mmol after seven hours.

The polymer obtained is recovered and analysed as in Example 3.1. The results are given in Table 12.

Example 3.4: p(St-b-MeA-b-St) block copolymer

The following are introduced into a 10 ml round-bottomed flask:

- 1 mmol of [1-(O-ethylxanthyl)ethyl]benzene (0.226 g) and
- 20 mmol of styrene (2.08 g).

The temperature is raised to 90°C and 0.03 mmol of lauroyl peroxide (12.8 mg) are added. The temperature is maintained at 90°C for 10 hours, during which several additions of initiator are made:

- 0.01 mmol after two hours,
- 0.01 mmol after four hours,
- 0.01 mmol after six hours,
- 0.01 mmol after eight hours.

Next, the reaction mixture is cooled to 80°C and the following are introduced:

- 20 mmol of methyl acrylate and
- 0.02 mmol of lauroyl peroxide.

This second step lasts 8 hours, during which several additions of initiator are made:

- 0.01 mmol after two hours,
- 0.01 mmol after four hours,
- 0.01 mmol after six hours,
- 0.01 mmol after seven hours.

The temperature is again raised to 90°C and the following are introduced:

- 20 mmol of styrene (2.08 g) and
- 0.02 mmol of lauroyl peroxide.

This third step lasts 8 hours, during which several additions of initiator are made:

- 1 mmol after two hours,
- 1 mmol after four hours,
- 1 mmol after six hours.

The polymer obtained is recovered and analysed as in Example 3.1. The results are given in Table 12.

Example 3.5: p(MeA-b-St) block copolymer

The following are introduced into a round-bottomed flask:

- 1 mmol of [1-(O-ethylxanthyl)ethyl]benzene (0.226 g) and

- 20 mmol of methyl acrylate (1.72 g).

The temperature is raised to 80°C and 0.02 mmol of lauroyl peroxide are added. This first step lasts 8 hours, during which several additions of initiator are made:

- 1 mmol after two hours,
- 1 mmol after four hours,
- 1 mmol after six hours.

Next, the temperature is increased to 90°C and the following are introduced:

- 20 mmol of styrene and
- 0.02 mmol of lauroyl peroxide. This second step lasts 14 hours, during which several additions of initiator are made:
- 0.01 mmol after two hours,
- 0.01 mmol after four hours,
- 0.01 mmol after six hours,
- 0.01 mmol after eight hours,
- 0.01 mmol after ten hours,
- 0.01 mmol after twelve hours.

The polymer obtained is recovered and analysed as in Example 3.1. The results are given in Table 12.

Example 3.6: p(EtA-b-MVA) block copolymer

The following are introduced into a round-bottomed flask:

- 1.881 g of ethyl acrylate,

- 0.111 g of ethyl α-(O-ethylxanthyl)propionate and
- 8.6 mg of lauroyl peroxide.

The temperature is raised to 80°C. The polymerization lasts 6 hours, during which several additions of lauroyl peroxide are made:

- 9.2 mg after 2 hours,
- 9.0 mg after 4 hours.

After cooling, the traces of residual ethyl acrylate are removed by evaporation under high vacuum and a small fraction of the polymer is taken for GPC analysis in THF medium and in polystyrene equivalents. The results are as follows:

- degree of conversion: 98.3%
- M_n = 2800
- PI = 1.8.

Next, 1.853 g of vinyl acetate and 8.6 mg of lauroyl peroxide are introduced into the flask. The temperature is raised to 80°C. The polymerization lasts 6 hours, during which several additions of lauroyl peroxide are made:

- 8.6 mg after 2 hours,
- 8.5 mg after 4 hours.

The traces of residual vinyl acetate are removed by evaporation under high vacuum. The results are given in Table 12.

Example 3.7: p(EtA-b-tBuA) block copolymer

The following are introduced into a round-

bottomed flask:

- 1.881 g of ethyl acrylate,
- 0.111 g of ethyl α-(O-ethylxanthyl)propionate and
- 9.0 mg of lauroyl peroxide. The temperature is raised to 80°C. The polymerization lasts 6 hours, during which several additions of lauroyl peroxide are made:
- 8.6 mg after 2 hours,
- 8.9 mg after 4 hours.

After cooling, the traces of residual ethyl acrylate are removed by evaporation under high vacuum and a small fraction of the polymer is taken to be analysed by GPC in THF medium and in polystyrene equivalents:

- degree of conversion: 98.6%
- M_n = 2600
- PI = 1.9.

Next, the following are introduced into the flask:

- 2.7467 g of *tert*-butyl acrylate and
- 8.5 mg of lauroyl peroxide.

The temperature is raised to 80°C. The polymerization lasts 6 hours, during which several additions of lauroyl peroxide are made:

- 8.7 mg after 2 hours,
- 8.5 mg after 4 hours.

The traces of residual *tert*-butyl acrylate are removed by evaporation under high vacuum and the copolymer obtained is analysed by GPC in THF medium and

in polystyrene equivalents. The results are given in Table 12.

Example 3.8: p(*t*-BuA-b-MVA) block copolymer

The following are introduced into a round-bottomed flask:

- 2.737 g of *tert*-butyl acrylate,
- 0.111 g of ethyl α-(O-ethylxanthyl)propionate and
- 8.7 mg of lauroyl peroxide.

The temperature is raised to 80°C. The polymerization lasts 6 hours, during which several additions of lauroyl peroxide are made:

- 8.9 mg after 2 hours,
- 8.9 mg after 4 hours.

After cooling, the residual traces of *tert*-butyl acrylate are removed by evaporation under high vacuum and a small fraction of the polymer is taken to be analysed by GPC in THF medium and in polystyrene equivalents:

- degree of conversion: 98.3%,
- M_n = 2500,
- PI = 2.4.

Next, the following are introduced into the flask:

- 1.851 g of vinyl acetate and
- 8.5 mg of lauroyl peroxide.

The temperature is raised to 80°C. The polymerization lasts 6 hours, during which several

additions of lauroyl peroxide are made:

- 8.7 mg after 2 hours,
- 8.5 mg after 4 hours.

The traces of residual vinyl acetate are removed by evaporation under high vacuum and the copolymer obtained is analysed by GPC in THF medium and in polystyrene equivalents. The results are given in Table 12.

Example 3.9: p(tBuA-b-EtA) block copolymer

The following are introduced into a round-bottomed flask:

- 2.737 g of *tert*-butyl acrylate,
- 0.111 g of ethyl -(O-ethylxanthyl)propionate and
- 8.4 mg of lauroyl peroxide.

The temperature is raised to 80°C. The polymerization lasts 6 hours, during which several additions of lauroyl peroxide are made:

- 9.0 mg after 2 hours,
- 8.7 mg after 4 hours.

After cooling, the residual traces of *tert*-butyl acrylate are removed by evaporation under high vacuum and a small fraction of the polymer is taken to be analysed by GPC in THF medium and in polystyrene equivalents:

- degree of conversion: 98.1%,
- M_n = 2500,
- PI = 2.5.

Next, the following are introduced into the flask:

- 1.896 g of ethyl acrylate and
- 8.8 mg of lauroyl peroxide.

The temperature is raised to 80°C. The polymerization lasts 6 hours, during which several additions of lauroyl peroxide are made:

- 8.7 mg after 2 hours,
- 8.5 mg after 4 hours.

The traces of residual ethyl acrylate are removed by evaporation under high vacuum and the copolymer obtained is analysed by GPC in THF medium and in polystyrene equivalents. The results are given in Table 12.

Example 3.10: p(EtA-b-St) block copolymer

The following are introduced into a round-bottomed flask:

- 1.881 g of ethyl acrylate,
- 0.111 g of ethyl α-(O-ethylxanthyl)propionate and
- 8.8 mg of lauroyl peroxide.

The temperature is raised to 80°C. The polymerization lasts 6 hours, during which several additions of lauroyl peroxide are made:

- 9.0 mg after 2 hours,
- 8.5 mg after 4 hours.

After cooling, the residual traces of ethyl acrylate are removed by evaporation under high vacuum

and a small fraction of the polymer is taken to be analysed by GPC in THF medium and in polystyrene equivalents:

- degree of conversion: 97.5%,
- M_n = 3000,
- PI = 1.8.

Next, the following are introduced into the flask:

- 2.231 g of styrene and
- 9.0 mg of lauroyl peroxide.

The temperature is raised to 115°C. The polymerization lasts 6 hours, during which several additions of lauroyl peroxide are made:

- 8.7 mg after 2 hours,
- 9.9 mg after 4 hours.

The traces of residual styrene are removed by evaporation under high vacuum and the copolymer obtained is analysed by GPC in THF medium and in polystyrene equivalents. The results are given in Table 12.

Example 3.11: p(*t*BuA-b-St) block copolymer

The following are introduced into a round-bottomed flask:

- 2.737 g of *tert*-butyl acrylate,
- 0.111 g of ethyl α-(O-ethylxanthyl)propionate and
- 9.0 mg of lauroyl peroxide.

The temperature is raised to 80°C. The

polymerization lasts 6 hours, during which several additions of lauroyl peroxide are made:

- 8.5 mg after 2 hours,
- 9.6 mg after 4 hours.

After cooling, the residual traces of *tert*-butyl acrylate are removed by evaporation under high vacuum and a small fraction of the polymer is taken to be analysed by GPC in THF medium and in polystyrene equivalents:

- degree of conversion: 98.4%,
- M_n = 2800,
- PI = 2.4.

Next, the following are introduced into the flask:

- 2.246 g of styrene and
- 8.4 mg of lauroyl peroxide.

The temperature is raised to 115°C. The polymerization lasts 6 hours, during which several additions of lauroyl peroxide are made:

- 9.2 mg after 2 hours,
- 9.2 mg after 4 hours.

The traces of residual styrene are removed by evaporation under high vacuum and the copolymer obtained is analysed by GPC in THF medium and in polystyrene equivalents. The results are given in Table 12.

Example 3.12: p(EtA-b-tBuA-b-St) block copolymer

The following are introduced into a round-bottomed flask:

- 2.248 g of styrene,
- the entire copolymer obtained in Example 3.7 and
- 8.3 mg of lauroyl peroxide.

The temperature is raised to 115°C. The polymerization lasts 6 hours, during which several additions of lauroyl peroxide are made:

- 9.0 mg after 2 hours,
- 8.5 mg after 4 hours.

The traces of residual styrene are removed by evaporation under high vacuum and the copolymer obtained is analysed by GPC in THF medium and in polystyrene equivalents. The results are given in Table 12.

Example 3.13: p(St-b-EtA) block copolymer

The following are introduced into a round-bottomed flask:

- 2.224 g of styrene,
- 0.111 g of ethyl α-(O-ethylxanthyl)propionate and
- 8.6 mg of lauroyl peroxide.

The temperature is raised to 115°C. The polymerization lasts 6 hours, during which several additions of lauroyl peroxide are made:

- 8.7 mg after 2 hours,
- 8.3 mg after 4 hours.

After cooling, the traces of residual styrene are removed by evaporation under high vacuum and a small fraction of the polymer is taken to be analysed by GPC in THF medium and in polystyrene equivalents:

- degree of conversion: 98.0%
- M_n = 3500,
- PI = 2.2.

Next, the following are introduced into the flask:

- 2 ml of toluene,
- 1.892 ? of ethyl acrylate and
- 8.5 mg of lauroyl peroxide.

The temperature is raised to 80°C. The polymerization lasts 6 hours, during which several additions of lauroyl peroxide are made:

- 9.4 mg after 2 hours,
- 9.2 mg after 4 hours.

The traces of residual ethyl acrylate are removed by evaporation under high vacuum and the copolymer obtained is analysed by GPC in THF medium and in polystyrene equivalents. The results are given in table 12.

Example 3.14: p(St-b-tBuA) block copolymer

The following are introduced into a round-bottomed flask:

- 2.224 g of styrene,
- 0.111 g of ethyl α-(O-ethylxanthyl)propionate and

- 8.6 mg of lauroyl peroxide.

The temperature is raised to 115°C. The polymerization lasts 6 hours, during which several additions of lauroyl peroxide are made:

- 8.7 mg after 2 hours,
- 9.5 mg after 4 hours.

After cooling, the traces of residual styrene are removed by evaporation under high vacuum and a small fraction of the polymer is taken to be analysed by GPC in THF medium and in polystyrene equivalents:

- degree of conversion: 97.2%
- M_n = 3400,
- PI = 2.2.

Next, the following are introduced into the flask:

- 2 ml of toluene,
- 2.747 g of *tert*-butyl acrylate and
- 9.3 mg of lauroyl peroxide.

The temperature is raised to 80°C. The polymerization lasts 6 hours, during which several additions of lauroyl peroxide are made:

- 8.7 mg after 2 hours,
- 9.3 mg after 4 hours.

The traces of residual *tert*-butyl acrylate are removed by evaporation under high vacuum and the copolymer obtained is analysed by GPC in THF medium and in polystyrene equivalents. The results are given in table 12.

Example 3.15: p(tBuA-b-EtA-b-St) block copolymer

The following are introduced into a round-bottomed flask:

- 2 ml of toluene,
- 2.229 g of styrene,
- the entire copolymer obtained in Example 3.9 and
- 9.1 mg of lauroyl peroxide.

The temperature is raised to 120°C. The polymerization lasts 6 hours, during which several additions of lauroyl peroxide are made:

- 8.5 mg after 2 hours,
- 8.5 mg after 4 hours.

The traces of residual styrene are removed by evaporation under high vacuum and the copolymer obtained is analysed by GPC in THF medium and in polystyrene equivalents. The results are given in Table 12.

Example 3.16: pBuA-b-PVA block copolymers (PVA: polyvinyl alcohol)

These copolymers are obtained by hydrolysing their p(BuA-b-MVA) equivalents.

A series of p(BuA-b-MVA) block copolymers is prepared. All the copolymers are obtained according to the following general operating method.

The following are introduced into a round-bottomed flask:

- butyl acrylate (BuA),

- ethyl α-(O-ethylxanthyl)propionate and
- approximately one third of the total amount of lauroyl peroxide necessary for this first step.

The temperature is raised to 80°C. The polymerization lasts 6 hours, during which two additions of initiator are made after 2 and 4 hours. Each of the additions corresponds to approximately one third of the total amount of lauroyl peroxide of the first step.

The traces of residual butyl acrylate are removed by evaporation and a small fraction of the polymer is taken to be analysed.

Next, the following are added to the flask:
- vinyl acetate and
- approximately one third of the total amount of lauroyl peroxide necessary for this second step.

The temperature is again raised to 80°C. The polymerization lasts 6 hours and the rest of the initiator is added in the same way as for the synthesis of the first block. The block copolymer is recovered after evaporating the traces of residual vinyl acetate and analysed by GPC in THF medium and in polystyrene equivalents.

The amounts of ingredients used for each of the copolymers, as well as the results obtained, are given in Table 11.

Table 11

Polymerization 1			Homopolymer		Polymerization 2		Block polymer	
BuA mass (g)	Precursor mass (g)	Perox. mass (mg)	M_n	PI	MVA mass (g)	Perox. mass (mg)	M_n	PI
13.713	1.126	0.257	2500	1.6	13.789	0.263	4500	1.4
13.695	1.125	0.257	2500	1.6	18.395	0.265	5300	1.4
19.158	0.791	0.347	3900	2.0	6.461	0.350	5600	1.7
19.157	0.798	0.360	3900	2.0	12.872	0.352	7200	1.6
19.242	1.568	0.370	2500	1.6	6.470	0.365	3200	1.5
19.295	1.568	0.371	2500	1.7	12.969	0.359	4100	1.4
6.71	1.067	0.246	1500	1.4	22.027	0.497	5900	1.5

Next, the block polymers obtained are hydrolysed: they are dissolved in methanol, with 50% solids content, and then a catalytic amount of sodium hydroxide is added and the reaction mixture is heated at 60°C for 1 hour.

The pBuA-b-PVA copolymers are recovered by evaporating the methanol.

Example 3.17: pAA-b-PVA block copolymer

This copolymer is obtained by hydrolysing the corresponding p(*t*BuA-b-MVA) copolymer.

The following are introduced into a round-bottomed flask:

- 2.737 g of *tert*-butyl acrylate,
- 0.111 g of ethyl α-(O-ethylxanthyl)propionate and
- 8.5 mg of lauroyl peroxide.

The temperature is raised to 80°C.

The polymerization lasts 6 hours, during which several additions of lauroyl peroxide are made:

- 9.5 mg after 2 hours,
- 9.8 mg after 4 hours.

After cooling, the traces of residual *tert*-butyl acrylate are removed by evaporation under high vacuum.

A small fraction of the polymer is taken to be analysed by GPC in THF medium and in polystyrene equivalents:

- degree of conversion: 99.0%,
- M_n = 4300,
- PI = 1.7.

Next, the following are introduced into the flask:

- 1.831 g of vinyl acetate and
- 8.6 mg of lauroyl peroxide.

The temperature is raised to 80°C.

The polymerization lasts 6 hours, during which several additions of lauroyl peroxide are made:

- 9.2 mg after 2 hours,
- 9.2 mg after 4 hours.

The traces of residual vinyl acetate are removed by evaporation under high vacuum and the copolymer obtained is analysed by GPC in THF medium and in polystyrene equivalents. The results are given in Table 12.

Next, the copolymer obtained is hydrolysed in the following manner.

The copolymer is introduced into a water/methanol (10 ml/4 ml) mixture. Three drops of 95% sulphuric acid are added so as to obtain a pH of 1. The temperature is raised to 70°C. After 2 hours 15 minutes, 8 ml of methanol are added and, after 5 hours, three new drops of 95% sulphuric acid are added. This first step lasts 24 hours and enables the poly(*tert*-butyl acrylate) block to be converted into polyacrylic acid.

Next, the temperature is returned to room temperature and the solvent (water + methanol) is removed by evaporation. The dry residue obtained is redissolved in 30 ml of methanol and a catalytic amount of NaOH is added. The temperature is again raised to 70°C, at which it is maintained for 24 hours.

The polyacrylic acid/polyvinyl alcohol copolymer obtained is recovered by evaporating the methanol.

Example 3.18: p(BuA-b-EtA) block copolymer

The following are introduced into a reactor fitted with a stirring system:

- 60 g of isopropyl acetate,
- 90 g of butyl acrylate and
- 6.9 g of ethyl α-(O-ethylxanthyl)propionate.

The temperature is raised to 80°C. 0.18 g of AIBN in solution in 5 g of isopropyl acetate are added in one go.

Fifteen minutes later, a solution containing:

- 180 g of isopropyl acetate,
- 274 g of butyl acrylate and
- 0.5 g of AIBN

is fed continuously over a period of 2 hours.

The temperature and stirring are maintained for 1 hour 45 minutes after the end of adding the first monomer.

A small fraction of the precursor polymer is taken and analysed by GPC in THF medium and in polystyrene equivalents:

- M_n = 7000,
- PI = 1.9.

A second continuous feed then takes place over a period of 1 hour. It consists of a solution containing:

- 10 g of isopropyl acetate,
- 163 g of ethyl acrylate and
- 0.32 g of AIBN.

The temperature and stirring are maintained for one further hour after the end of adding the second monomer.

The final copolymer is obtained by evaporating the solvent and the traces of residual monomers and is analysed by GPC in THF medium and in polystyrene equivalents. The results are given in Table 12.

Example 3.19: p(BuA-b-EtA) block copolymer

The following are introduced into a reactor fitted with a stirring system:

- 45 g of isopropyl acetate,
- 75 g of butyl acrylate and
- 6.9 g of ethyl α-(O-ethylxanthyl)propionate.

The temperature is raised to 80°C and 0.15 g of AIBN in solution in 5 g of isopropyl acetate are added in one go.

Twenty minutes later, a solution containing:

- 117 g of isopropyl acetate,
- 175 g of butyl acrylate and
- 0.35 g of AIBN

is fed continuously over a period of 1 hour 30 minutes.

The temperature and stirring are maintained for 2 hours 10 minutes after the end of adding the first monomer.

A small fraction of the precursor polymer is taken and analysed by GPC in THF medium and in polystyrene equivalents:

- M_n = 5200
- PI = 1.8.

A second continuous feed is then carried out

over a period of 1 hour 40 minutes. It consists of a solution containing:

- 168 g of isopropyl acetate,
- 252 g of ethyl acrylate and
- 0.5 g of AIBN.

The temperature and stirring are maintained for a further 20 minutes after the end of adding the second monomer.

The final copolymer is recovered by evaporating the solvent and the traces of residual monomers and is analysed by GPC in THF medium and in polystyrene equivalents. The results are given in Table 12.

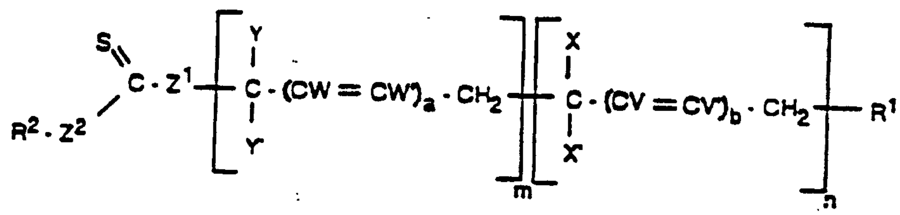
Results of Examples 3.1 to 3.19

Table 12

Examples	Monomers			M_n	PI	Degree of conversion
	M1	M2	M3			
Ex. 3.1	MeA	St	-	4650	1.6	
Ex. 3.2	St	MeA	-	4300	1.7	
Ex. 3.3	St	MeA	-	4200	1.8	
Ex. 3.4	St	MeA	St	6200	2	
Ex. 3.5	MeA	St	-	3750	1.8	
Ex. 3.6	EtA	MVA	-	5600	1.4	92.3%
Ex. 3.7	EtA	tBuA	-	6800	1.7	97.8%
Ex. 3.8	tBuA	MVA	-	6900	1.5	83.8%
Ex. 3.9	tBuA	EtA	-	7000	2.0	96.1%
Ex. 3.10	EtA	St	-	7600	1.8	98.4%
Ex. 3.11	tBuA	St	-	8100	2.9	95.9%
Ex. 3.12	EtA	tBuA	St	13,000	2.4	97.5%
Ex. 3.13	St	EtA	-	6200	1.9	> 99%
Ex. 3.14	St	tBuA	-	7100	1.9	> 99%
Ex. 3.15	tBuA	EtA	St	11,400	2.4	> 99%
Ex. 3.17	tBuA	MVA	-	7400	1.4	88%
Ex. 3.18	BuA	EtA	-	8700	2.2	95%
Ex. 3.19	Bua	EtA	-	10,000	2.0	80%

CLAIMS

1. Process for preparing block polymers of general formula (I):



(I)

in which:

- Z^1 = S or P,
- Z^2 = O, S or P,
- R^1 and R^2, which are identical or different, represent:
  - . an optionally substituted alkyl, acyl, aryl, alkene or alkyne group (i),

  or

  - . an optionally substituted, saturated or unsaturated, carbon or aromatic ring (ii),

  or

  - . an optionally substituted, saturated or unsaturated heterocycle (iii),

  it being possible for these groups and rings (i), (ii) and (iii) to be substituted with substituted phenyl groups, substituted aromatic groups, or groups: alkoxycarbonyl or aryloxycarbonyl (-COOR), carboxy (-COOH), acyloxy ($-O_2CR$), carbamoyl ($-CONR_2$), cyano (-CN), alkylcarbonyl, alkylarylcarbonyl, arylcarbonyl, arylalkylcarbonyl, phthalimido, maleimido, succinimido, amidino, guanidimo, hydroxyl

(-OH), amino ($-NR_2$), halogen, allyl, epoxy, alkoxy (-OR), S-alkyl, S-aryl, groups having a hydrophilic or ionic character, such as the alkali metal salts of carboxylic acids, the alkali metal salts of sulphonic acid, polyalkylene oxide chains (PEO, PPO), cationic substituents (quaternary ammonium salts),

R representing an alkyl or aryl group,

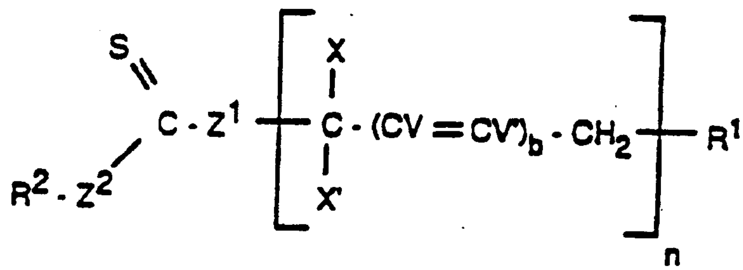
. a polymer chain,

- V, V', W and W', which are identical or different, represent: H, an alkyl group or a halogen,
- X, X', Y and Y', which are identical or different, represent H, a halogen or an R^3, OR^3, O_2COR^3, NHCOH, OH, NH_2, NHR^3, $N(R^3)_2$, $(R^3)_2N^+O^-$, $NHCOR^3$, CO_2H, CO_2R^3, CN, $CONH_2$, $CONHR^3$ or $CONR^3_2$ group, in which R^3 is chosen from alkyl, aryl, aralkyl, alkaryl, alkene or organosilyl groups, optionally perfluorinated and optionally substituted with one or more carboxyl, epoxy, hydroxyl, alkoxy, amino, halogen or sulphonic groups,
- a and b, which are identical or different, are equal to 0 or 1,
- m and n, which are identical or different, are greater than or equal to 1 and, when one or other is greater than 1, the individual repeat units are identical or different,

in which process the following are brought into contact with each other:

- an ethylenically unsaturated monomer of formula: $CYY'(=CW-CW')_a=CH_2$,

- a precursor compound of general formula (II):



(II)

- a radical polymerization initiator.

2. Process according to claim 1, characterized in that the ethylenically unsaturated monomer is chosen from: styrene or its derivatives, butadiene, chloroprene, (meth)acrylic esters, and vinylnitriles.

3. Process according to the preceding claim, characterized in that the ethylenically unsaturated monomer is chosen from vinylacetate, vinylversatate and vinylpropionate.

4. Process according to any one of the preceding claims, characterized in that R^1 represents:

- a group of formula $CR'^1R'^2R'^3$, in which:
  - . R'^1, R'^2 and R'^3 represent groups (i), (ii) or (iii) as defined above, or
  - . $R'^1 = R'^2 = H$ and R'^3 is an aryl, alkene or alkyne group,
- or a $-COR'^4$ group in which R'^4 represents a group (i), (ii) or (iii).

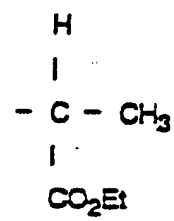
5. Process according to any one of the preceding claims, characterized in that R^2 represents a group of formula: $-CH_2R'^5$, in which R'^5 represents H or

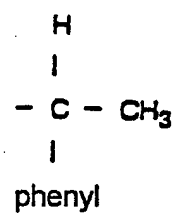
a group (i), (ii) or (iii) with the exception of aryl, alkyne and alkene groups.

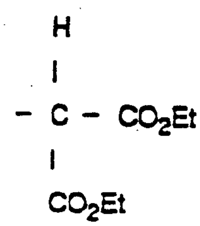
6. Process according to one of the preceding claims, characterized in that Z^1 is a sulphur atom and Z^2 is an oxygen atom.

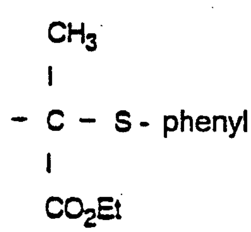
7. Process according to the preceding claim, characterized in that:

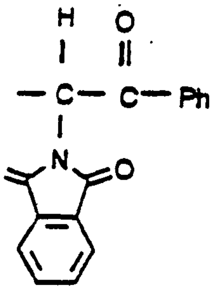
- R^1 is chosen from the groups:









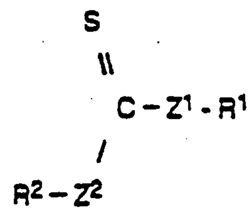


- and R^2 is an ethyl or phenyl group.

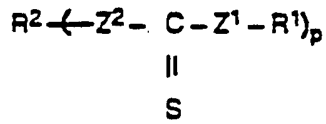
8. Process according to one of the preceding claims, characterized in that the compounds (II) are chosen from styrene (Y′ = H, Y = C_6H_5, b = 0), methyl acrylate (Y′ = H, Y = COOMe, b = 0), ethyl acrylate (Y′ = H, Y = COOEt, b = 0), butyl acrylate (Y′ = H, Y = COOBu, b = 0), *tert*-butyl acrylate (Y′ = H, Y = COOtBu, b = 0), vinyl acetate (Y′ = H, Y = OCOMe, b = 0) and acrylic acid (Y′ = H, Y = COOH, b = 0) homopolymers, for which:

- Z^1 = S, Z^2 = O, R^1 = CHCH3(CO_2Et) and R^2 = Et, or
- Z^1 = S, Z^2 = O, R^1 = CH(CO_2Et)$_2$ and R^2 = Et.

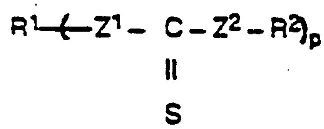
9. Process according to any one of the preceding claims, characterized in that the precursor compound of general formula (II) is a polymer and in that the said polymer comes from the radical polymerization of an ethylenically unsaturated monomer of formula: CXX′(=CV-CV′)$_b$=CH_2, during which polymerization the said monomer is brought into contact with a radical polymerization initiator and a compound of general formula (III), (IV) or (V):



(III)



(IV)



(V)

p being between 2 and 10.

10. Process according to the preceding claim, characterized in that the compound (III) is chosen from ethyl-α-(O-ethylxanthyl)propionate (Z^1 = S, Z^2 = O, R^1 = $CH(CH_3)(CO_2Et)$, R^2 = Et) and [1-(O-ethylxanthyl)malonate (Z^1 = S, Z^2 = O, R^1 = $CH(CO_2Et)_2$, R^2 = Et).

11. Process for preparing block polymers, characterized in that the implementation of the process according to one of claims 1 to 10 is repeated at least once, using:

- different monomers from those in the previous implementation, and
- instead of the precursor compound of formula (II), the block polymer coming from the previous implementation.

12. Block polymer which can be obtained by

the process according to one of claims 1 to 10 or 11.

13. Block polymer according to the preceding claim, characterized in that it has a polydispersity index of at most 2.

14. Block polymer according to claim 12 or 13, characterized in that it has a polydispersity index of at most 1.5.

15. Block polymer according to any one of claims 12 to 14, characterized in that it is of general formula (I) in which Z^1 is a sulphur atom and Z^2 is an oxygen atom.

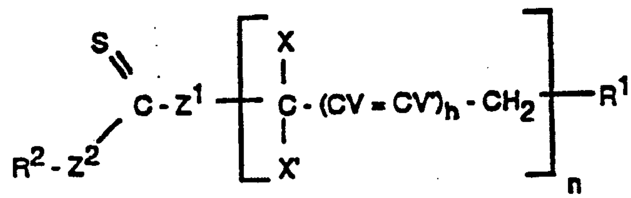
16. Block polymer according to any one of claims 12 to 15, characterized in that they have at least two polymer blocks chosen from the following combinations:

- polystyrene/polymethyl acrylate
- polystyrene/polyethyl acrylate,
- polystyrene/poly(*tert*-butyl acrylate),
- polyethyl acrylate/polyvinyl acetate,
- polybutyl acrylate/polyvinyl acetate,
- polyethyl acrylate/poly(*tert*-butyl acrylate),
- poly(*tert*-butyl acrylate)/polyvinyl acetate,
- polyethyl acrylate/polybutyl acrylate,
- polybutyl acrylate/polyvinyl alcohol,
- polyacrylic acid/polyvinyl alcohol.

17. Block polymer according to claim 16, characterized in that it is of general formula (I), in which:

- $Z^1 = S$, $Z^2 = O$, $R^1 = CHCH3(CO_2Et)$ and $R^2 = Et$, or
- $Z^1 = S$, $Z^2 = O$, $R^1 = CH(CO_2Et)_2$ and $R^2 = Et$.

18. Compound of general formula (II):



(II)

characterized in that it has a polydispersity index of at most 2.

19. Compound of general formula (II) according to the preceding claim, characterized in that it has a polydispersity index of at most 1.5.

20. Compound of general formula (II) according to the preceding claim, characterized in that Z^1 is a sulphur atom, Z^2 is an oxygen atom and n is greater than or equal to 6.

21. Compound of general formula (II) according to Claim 19 or 20, characterized in that it is chosen from styrene ($Y' = H$, $Y = C_6H_5$, $b = 0$), methyl acrylate ($Y' = H$, $Y = COOMe$, $b = 0$), ethyl acrylate ($Y' = H$, $Y = COOEt$, $b = 0$), butyl acrylate ($Y' = H$, $Y = COOBu$, $b = 0$), *tert*-butyl acrylate ($Y' = H$, $Y = COOtBu$, $b = 0$), vinyl acetate ($Y' = H$, $Y = OCOMe$, $b = 0$) and acrylic acid ($Y' = H$, $Y = COOH$, $b = 0$) polymers, for which:

- $Z^1 = S$, $Z^2 = O$, $R^1 = CH(CH3)(CO_2Et)$ and $R^2 = Et$, or
- $Z^1 = S$, $Z^2 = O$, $R^1 = CH(CO_2Et)_2$ and $R^2 = Et$.

DATED THIS 23RD DAY OF JUNE 1998

JOHN & KERNICK
FOR THE APPLICANT